

(12) **United States Patent**  
**Feser et al.**

(10) **Patent No.:** **US 9,739,729 B2**  
(45) **Date of Patent:** **\*Aug. 22, 2017**

(54) **COMBINED CONFOCAL X-RAY FLUORESCENCE AND X-RAY COMPUTERISED TOMOGRAPHIC SYSTEM AND METHOD**

(71) Applicant: **Carl Zeiss X-ray Microscopy, Inc.**, Pleasanton, CA (US)

(72) Inventors: **Michael Feser**, Orinda, CA (US); **Srivatsan Seshadri**, San Ramon, CA (US)

(73) Assignee: **Carl Zeiss X-ray Microscopy, Inc.**, Pleasanton, CA (US)

(\* ) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 0 days.

This patent is subject to a terminal disclaimer.

(21) Appl. No.: **14/425,573**

(22) PCT Filed: **Sep. 6, 2013**

(86) PCT No.: **PCT/US2013/058464**

§ 371 (c)(1),

(2) Date: **Mar. 3, 2015**

(87) PCT Pub. No.: **WO2014/039793**

PCT Pub. Date: **Mar. 13, 2014**

(65) **Prior Publication Data**

US 2015/0253263 A1 Sep. 10, 2015

**Related U.S. Application Data**

(60) Provisional application No. 61/698,137, filed on Sep. 7, 2012.

(51) **Int. Cl.**

**G01N 23/00** (2006.01)

**G01N 23/223** (2006.01)

(Continued)

(52) **U.S. Cl.**

CPC ..... **G01N 23/223** (2013.01); **G01N 23/046** (2013.01); **G01N 23/2206** (2013.01); (Continued)

(58) **Field of Classification Search**

CPC ..... G01N 2223/076; G01N 23/2206; G01N 23/223; G01N 2223/419; G01N 23/046; G01N 33/24

See application file for complete search history.

(56) **References Cited**

U.S. PATENT DOCUMENTS

5,192,869 A 3/1993 Kumakhov  
5,497,008 A 3/1996 Kumakhov  
(Continued)

FOREIGN PATENT DOCUMENTS

JP H05 060702 A 3/1993  
JP 2004138461 A 5/2004  
(Continued)

OTHER PUBLICATIONS

Woll et al. "Development of confocal X-ray fluorescence (XRF) microscopy at the Cornell high energy synchrotron source." 2006. Applied Physics A.\*

(Continued)

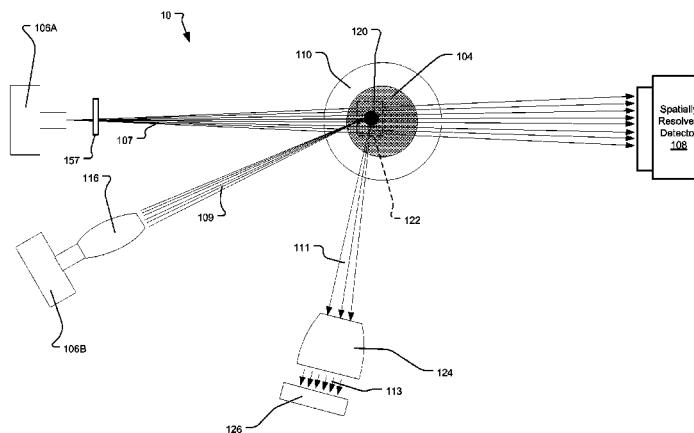
*Primary Examiner* — Dani Fox

(74) *Attorney, Agent, or Firm* — HoustonHogle LLP

(57) **ABSTRACT**

A correlative evaluation of a sample (104) using a combined x-ray computed tomography (CT) and x-ray fluorescence (XRF) system and the method for analyzing a sample (104) using x-ray CT and XRF is disclosed. The CT/XRF system (10) includes an x-ray CT subsystem (100) for acquisition of volume information and a confocal XRF subsystem (102) for characterization of elemental composition information. Geometrical calibration is carried out between the XRF subsystem (102) and the X-ray CT subsystem (100) such

(Continued)



that a region of interest defined during X-ray CT acquisition can be retrieved by the XRF subsystem (102) for a subsequent XRF acquisition. The system (10) combines the sub-micrometer spatial resolution 3-D imaging capability of x-ray CT with the elemental composition analysis of confocal XRF to provide 3-D elemental composition analysis of a sample (104) with ppm level sensitivity. This is applicable to many scientific research and industrial applications, a prime example of which is the elemental identification of precious metal grains in crushed and ground ores and floatation tailings in the mining industry.

### 18 Claims, 16 Drawing Sheets

- (51) **Int. Cl.**  
**G01N 23/22** (2006.01)  
**G01N 33/24** (2006.01)  
**G01N 23/04** (2006.01)
- (52) **U.S. Cl.**  
 CPC ..... **G01N 33/24** (2013.01); **G01N 2223/076**  
 (2013.01); **G01N 2223/419** (2013.01)

### (56) References Cited

#### U.S. PATENT DOCUMENTS

5,604,353	A	2/1997	Gibson et al.	
6,697,454	B1	2/2004	Nicolich et al.	
2007/0286339	A1*	12/2007	Rothschild .....	G01N 23/046 378/57
2009/0046832	A1*	2/2009	Birnbaum .....	G01N 23/2204 378/45
2011/0188629	A1	8/2011	Meng	
2013/0251100	A1*	9/2013	Sasaki .....	G01N 23/046 378/20
2014/0376685	A1*	12/2014	Koroteev .....	G01N 33/24 378/4

#### FOREIGN PATENT DOCUMENTS

JP	2010025711	A	2/2010
JP	2013224923	A	10/2013
WO	96/27194	A1	9/1996

#### OTHER PUBLICATIONS

Malzer, Wolfgang. "3D Micro X-ray Fluorescence Analysis." The Raigaku Journal, vol. 23 (2006), 40-47.\*  
 International Preliminary Report on Patentability, mailed Mar. 19, 2015, from counterpart International Application No. PCT/US2013/058464, filed Sep. 6, 2013.  
 Boone, M. et al., "3D Petrography of a Cu—Ba Mineralization by Combining muCT and muXRF", Proceedings of the 2011 International Association for Mathematical Geosciences Conference, Sep. 9, 2011, 2 pages.  
 De Samber, B. et al., "Element-to-Tissue Correlation in Biological Samples Determined by Three-Dimensional X-Ray Imaging Methods," Journal of Analytical Atomic Spectrometry, 2010, 25, pp. 544-553.  
 Fitzgerald, S. "Micro-Spectroscopy-Shedding Light on Rock Formation," <http://www.spectroscopyeurope.com>, vol. 17:3, pp. 24-25, 2005.  
 Harmful Element Fluorescence X-Ray Inspection Instrument, <http://www.horiba.com>, 4 pgs., 2003.  
 Havrilla, G.J. et al., "Dual-Polycapillary Micro X-Ray Fluorescence Instrument," 51st Annual Denver X-Ray Conf., 2002, 1 pg.

Janssens, K. et al., "Minimum Detectable Amounts and Minimum Detection Limits of Normal and confocal u-XRF at Hasylab BL L in Pink Beam Mode," HASYLAB, 2003, 2 pgs.  
 Liu, X. et al., "Calibration of Combined Laboratory MicroCT/MicroXRF System," Proceedings of the Conference of Developments in X-Ray Tomography VIII, vol. 8506, 850615, Aug. 12, 2012, 8 pages.  
 Markowicz, A. "Activities in the IAEA XRF Laboratory," XRF Newsletter, Issue No. 17, Jul. 2009.  
 Micro-XRF Analysis for Geological Applications, XRF Application Notes—<http://www.horiba.com>, 2005.  
 Miller, J. D. et al., "Liberation-Limited Grade/Recovery Curves from X-Ray Micro CT Analysis of Feed Material for the Evaluation of Separation Efficiency," International Journal of Mineral Processing, 2009, vol. 93, 48-53.  
 Patterson, B. et al., "Integrating 3D Images Using Laboratory-Based Micro X-Ray Computed Tomography and Confocal X-Ray Fluorescence Techniques," X-Ray Spectrometry, vol. 39, No. 3, May 1, 2010, pp. 184-190.  
 Sasov, A. et al., "A Compact MicroCT/MicroXRF Scanner for Non-Destructive 3D Chemical Analysis," Proceedings on the Conference on Developments in X-Ray Tomography VI, vol. 7078, 70780R, Aug. 28, 2008, 9 pages.  
 Schmitz, S. et al., "Chemical U—Th—Pb Dating of Monazite by 3D-Micro X-ray Fluorescence Analysis with Synchrotron Radiation," GFZ, 46 pgs., 2009.  
 Scott, D. et al., "High Resolution 3D Tomography for Advanced Package Failure Analysis," Xradia, Inc., 2006, 6 pgs.  
 Sparks, C.J. et al., "X-Ray Fluorescence Microprobe for Chemical Analysis," Synchrotron Radiation Research, 1980, pp. 459-512.  
 Stock, S.R., Recent Advances in X-Ray Microtomography Applied to Materials, Int. Mater Rev., 2008, vol. 1008:53, pp. 129-181.  
 Thermo Scientific Niton XRF Analyzers, <http://thermoscientific.com/niton>, 10 pgs., 2011.  
 Vekemans, B. "Polycapillary Based Confocal Detection Schemes for Micro and Nano-Spectroscopy," XMI—Department of Analytical Chemistry, Ghent University, Belgium, 30 pgs., 2009.  
 Vincze, L. et al., "X-ray Fluorescence Microtomography and Polycapillary Based Confocal Imaging Using Synchrotron Radiation," Developments in X-Ray Tomography IV, Proc. of SPIE vol. 5535, pp. 220-231, 2004.  
 Woll, A.R. et al. "Development of Confocal X-Ray Fluorescence (XRF) Microscopy at the Cornell High Energy Synchrotron Source," Applied Physics A, 2006, pp. 235-238.  
 X-Ray Analytical Microscope, <http://www.horiba.com>, 8 pgs., 2009.  
 Partial International Search Report from International Application No. PCT/US2013/058464, mailed on Nov. 25, 2013.  
 International Search Report and Written Opinion of the International Searching Authority mailed Feb. 3, 2014 from counterpart International Application No. PCT/US2013/058464, filed Sep. 6, 2013.  
 De Samber, B. et al., "Three-Dimensional Elemental Imaging by Means of Synchrotron Radiation Micro-XRF: Developments and Applications in Environmental chemistry," Anal. Bioanal., Chem., 2008, 390:267-271.  
 Havrilla, G. J. et al., "Confocal X-Ray Fluorescence Microscope Status and Future," HLW Workshop—SRNL, Jan. 19-21, 2005, 28 pgs.  
 Janssens, K. et al., "Confocal Microscopic X-Ray Fluorescence at the HASYLAB Microfocus Beamline: Characteristics and Possibilities," Spectrochimica Acta, Part B, 2004, vol. 59, pp. 1637-1645.  
 Malzer, "3D Micro X-Ray Fluorescence Analysis," The Rigaku Journal, vol. 23, 2006, pp. 40-47.  
 Wang, Y., et al., "A Novel X-ray Microtomography System with High Resolution and Throughput," NSTI-Nanotech, 3:503-507 (2004). Five pages.  
 Bruyndonckx, P. et al., "Progress in development of a laboratory microXRF-microCT system," Proceedings of SPIE—The International Society of Optical Engineering, vol. 7804, No. 78041A-1, Dec. 31, 2010. Ten pages.

\* cited by examiner

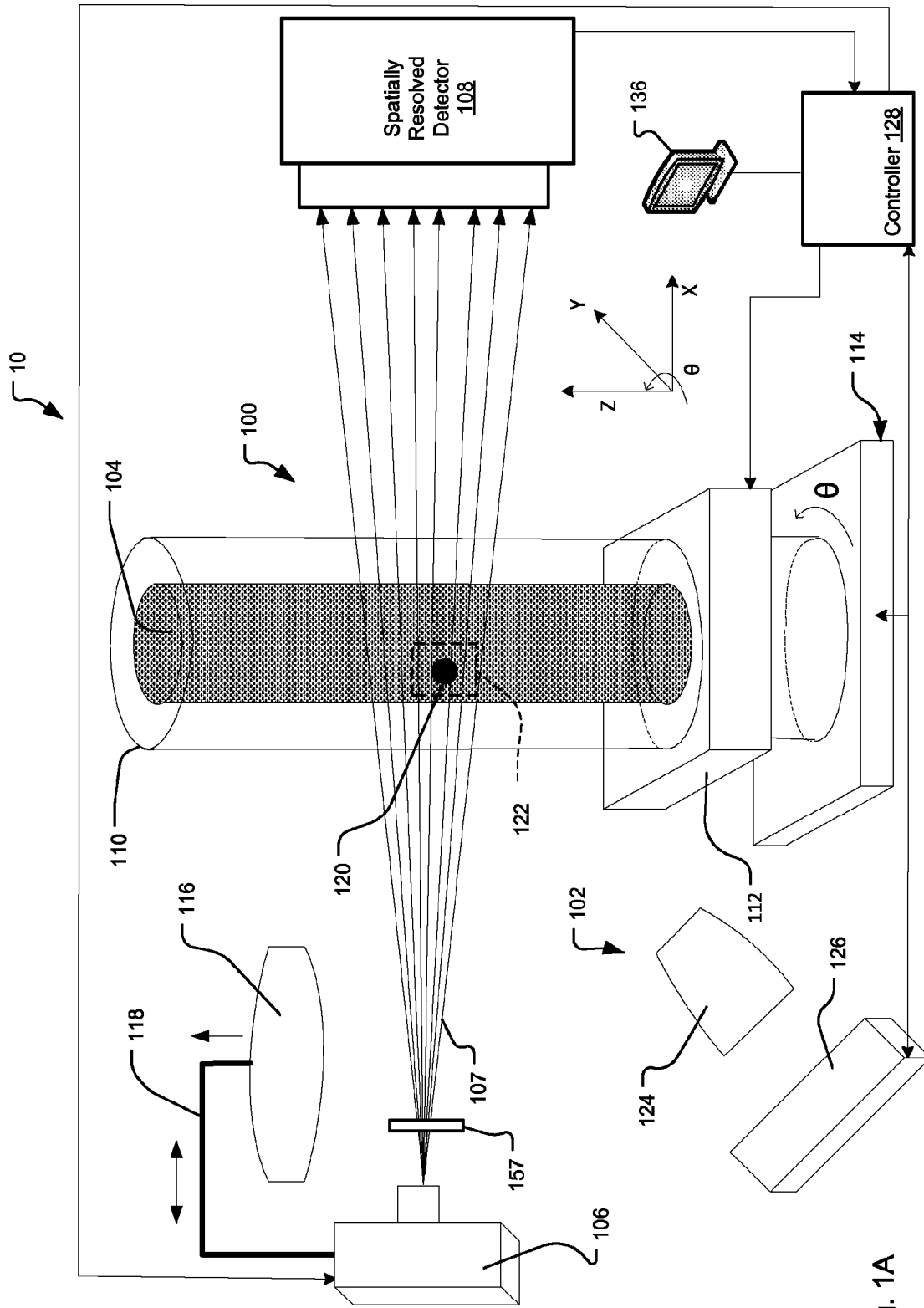


Fig. 1A



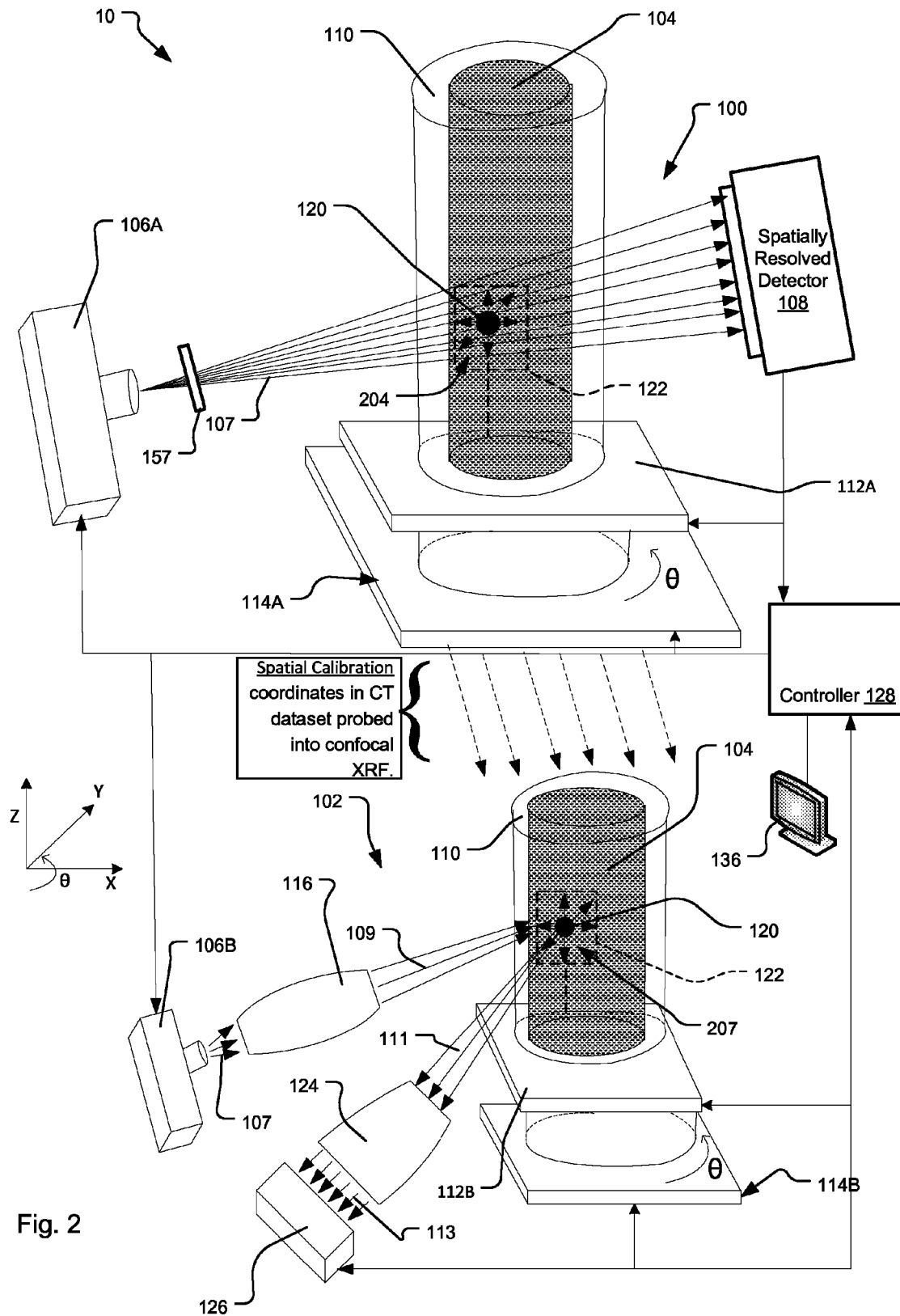


Fig. 2

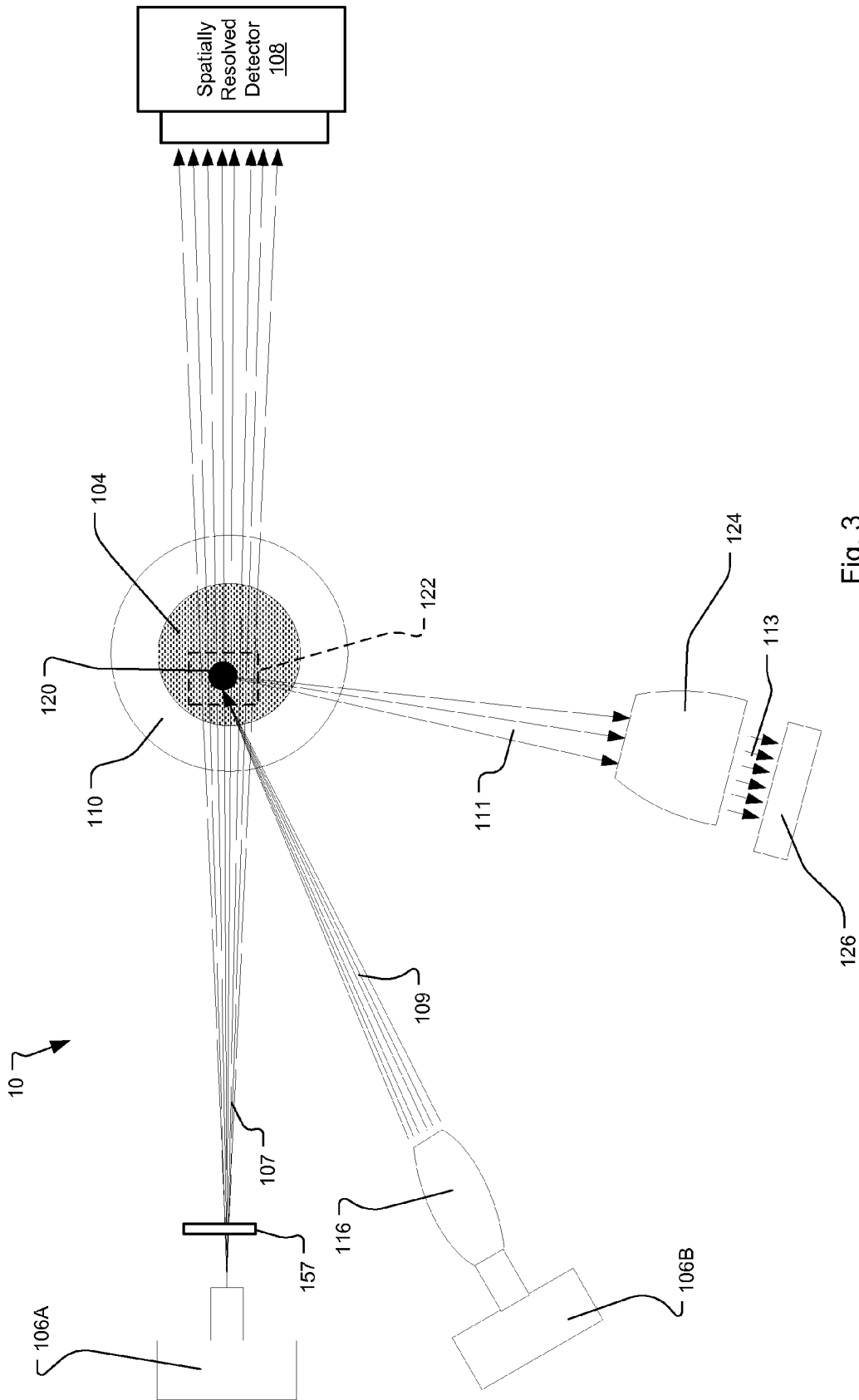


Fig. 3

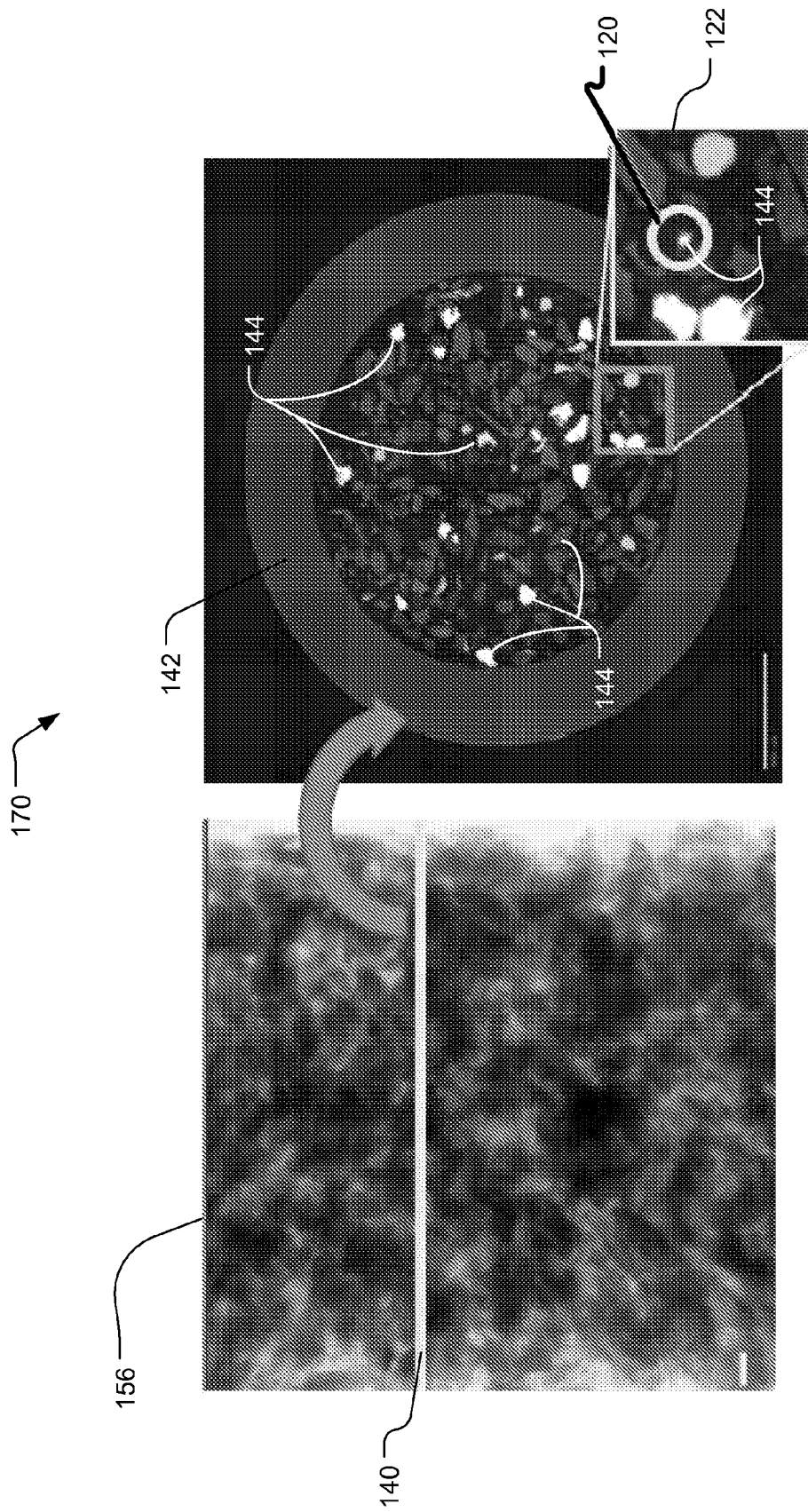


Fig. 4

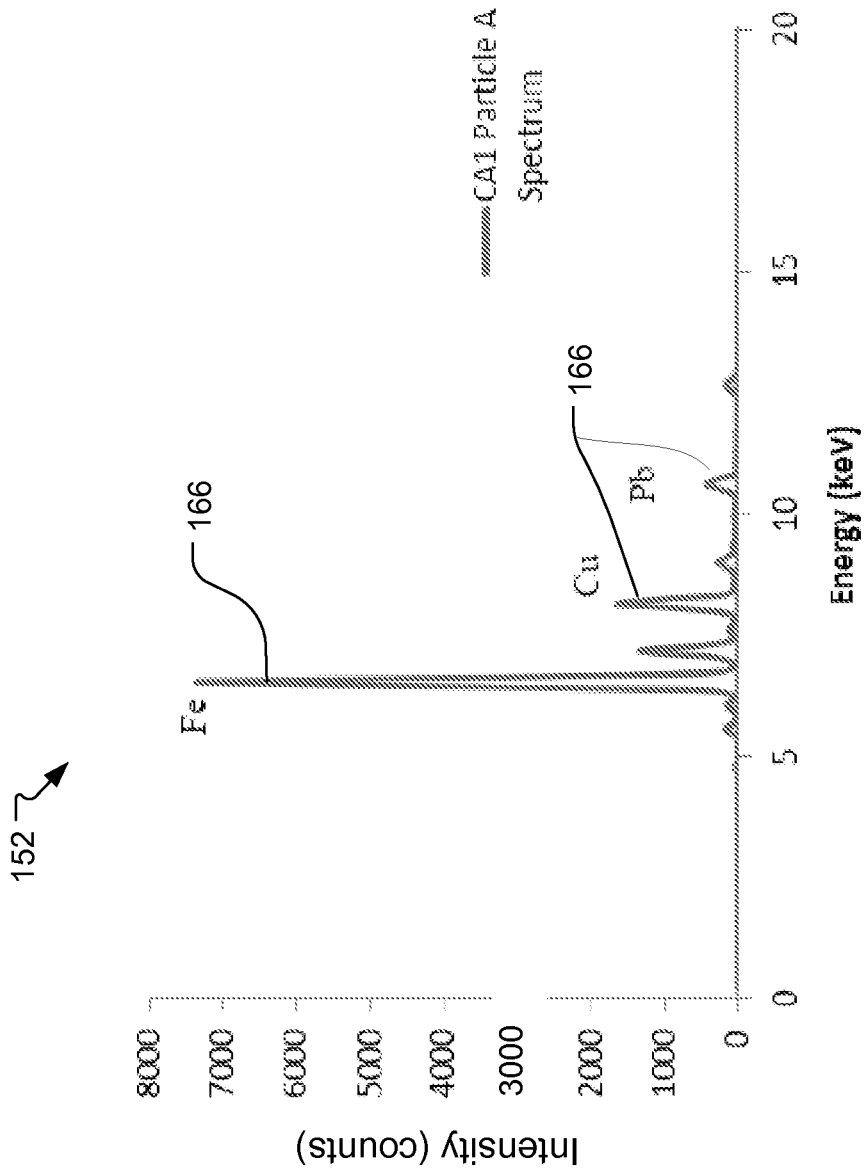


Fig. 5

152 ↗

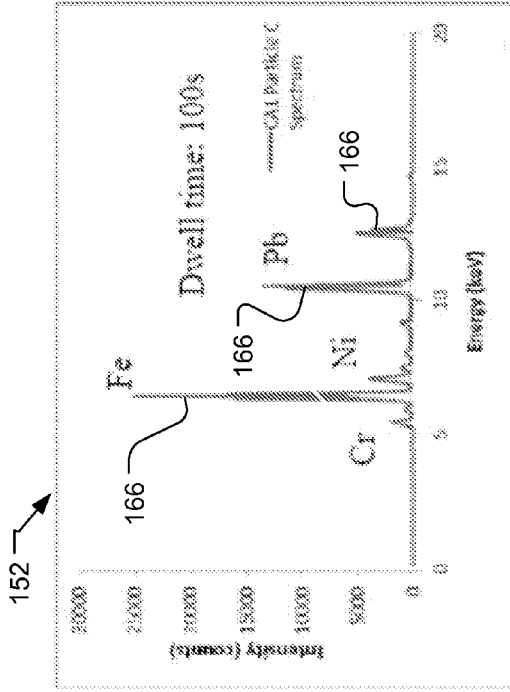


Fig. 6B

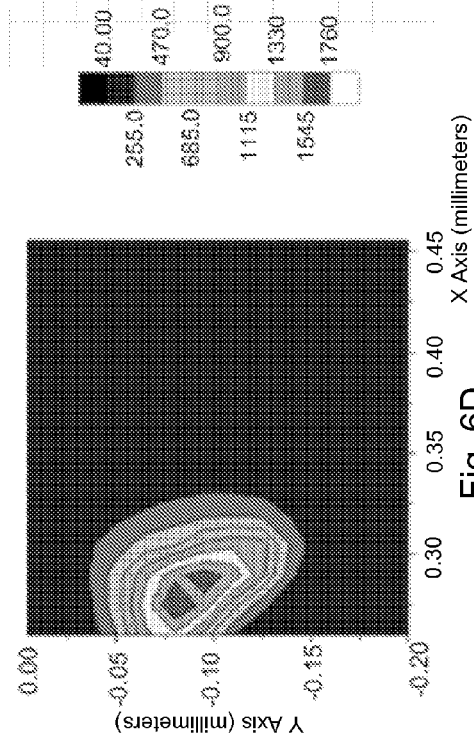


Fig. 6D

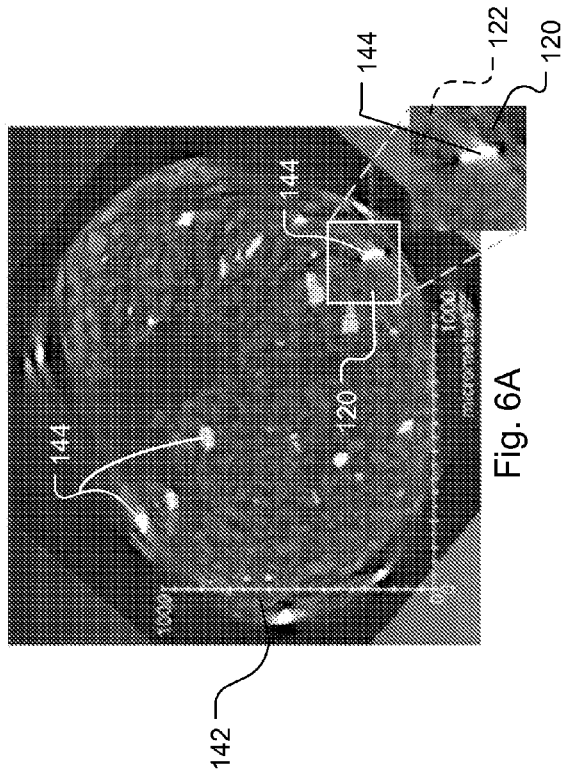


Fig. 6A

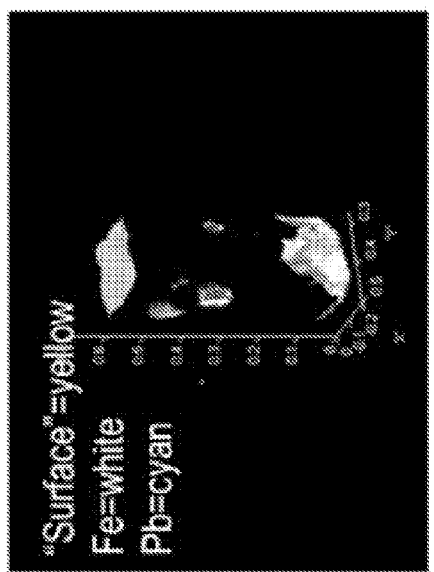


Fig. 6C

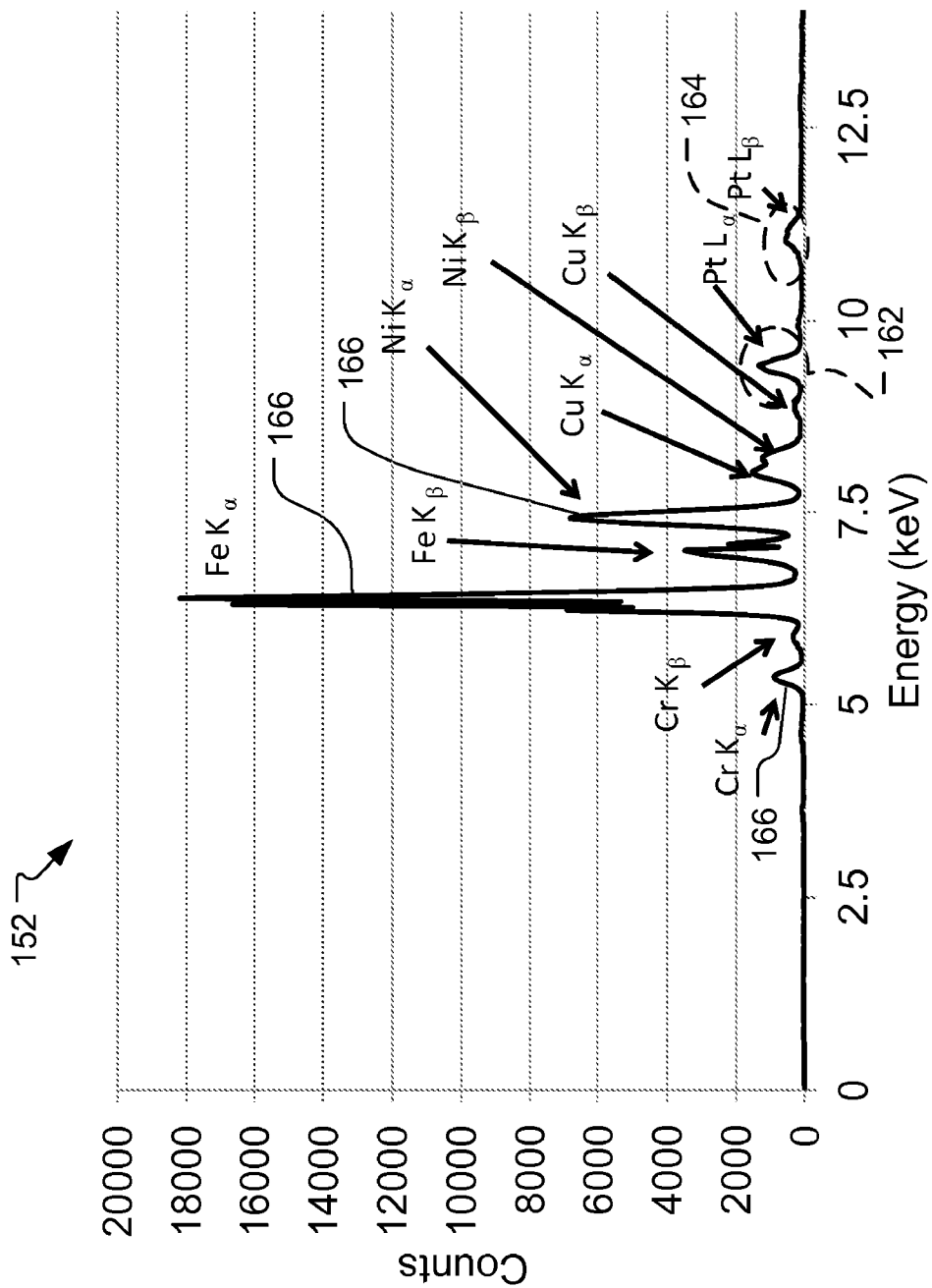


Fig. 7

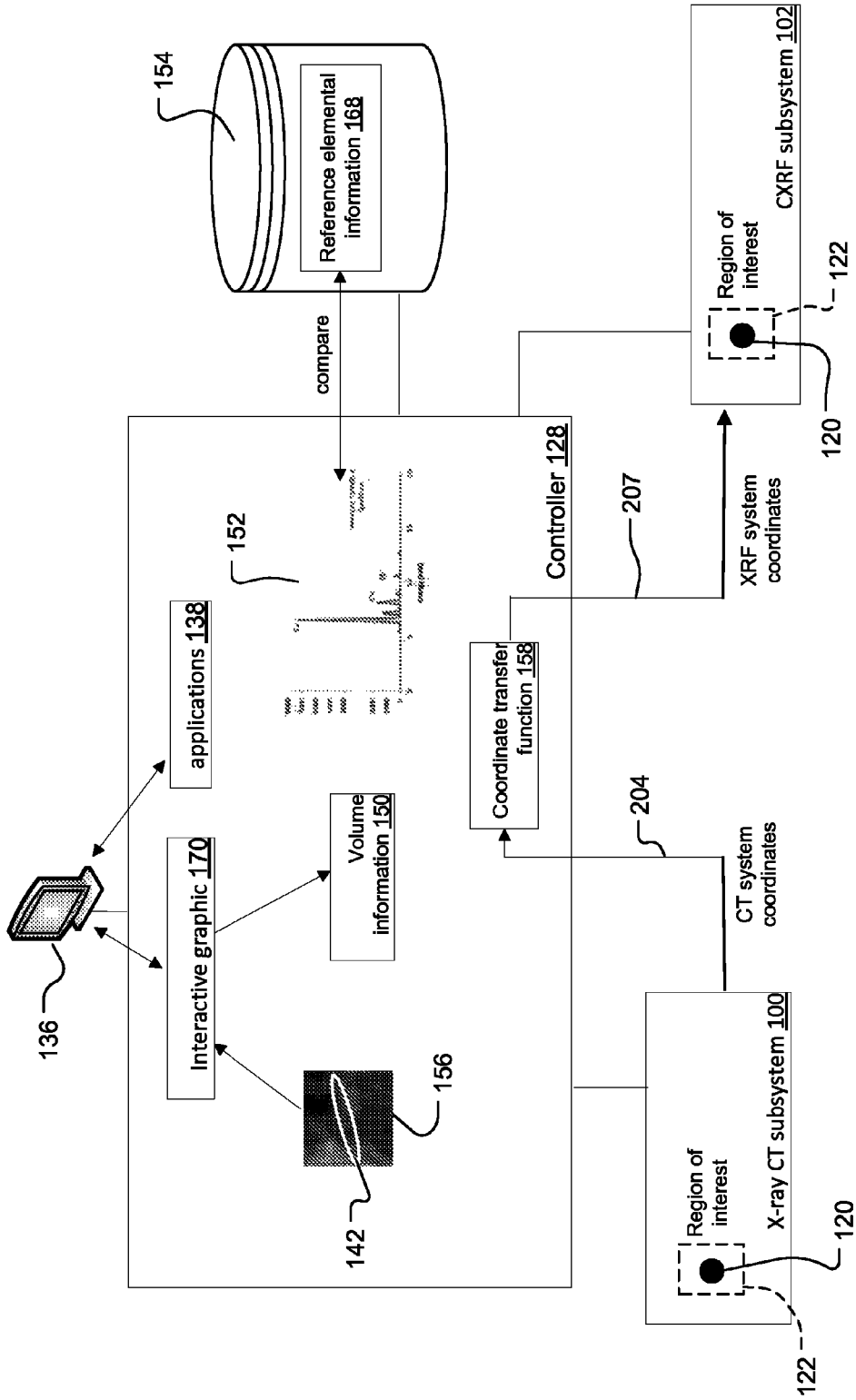


Fig. 8

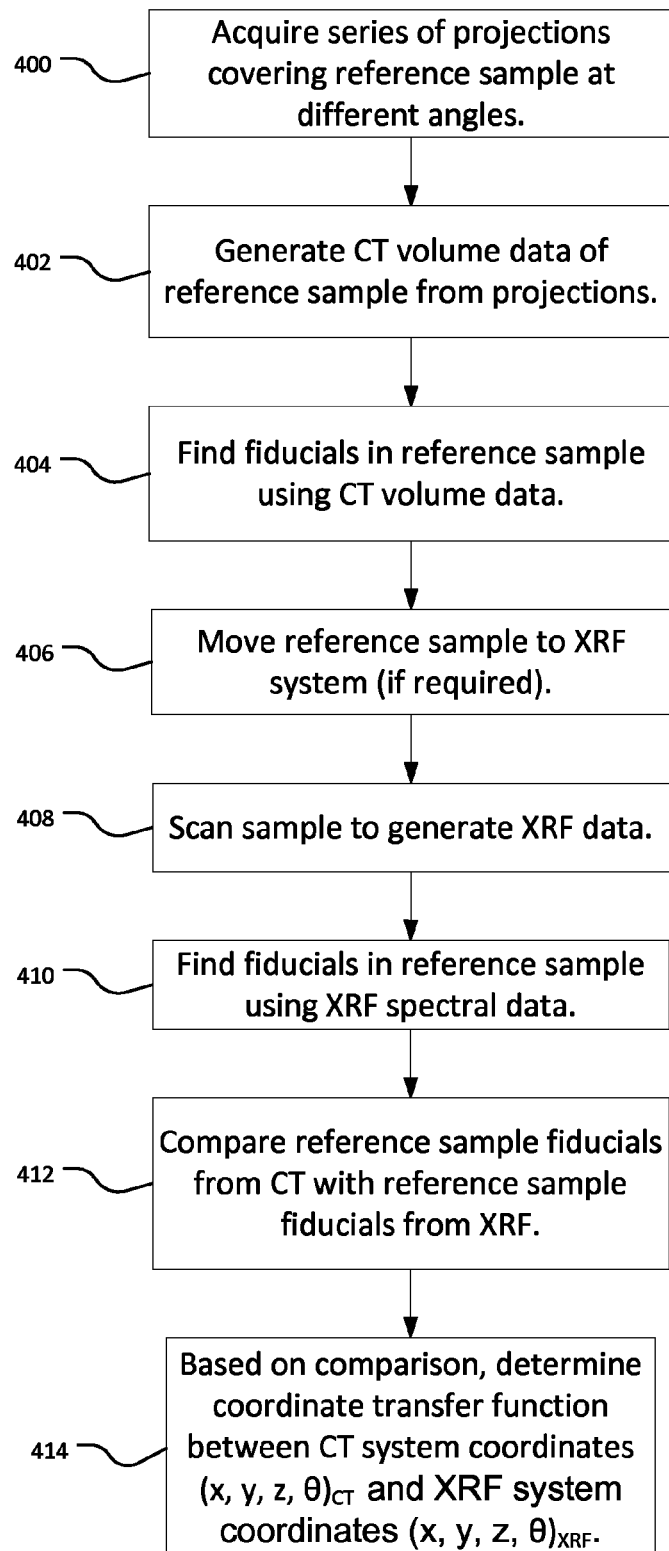
X-ray CT/XRF System Calibration Method

Fig. 9

Method for acquiring and preparing mineral material for X-ray  
CT/XRF system analysis

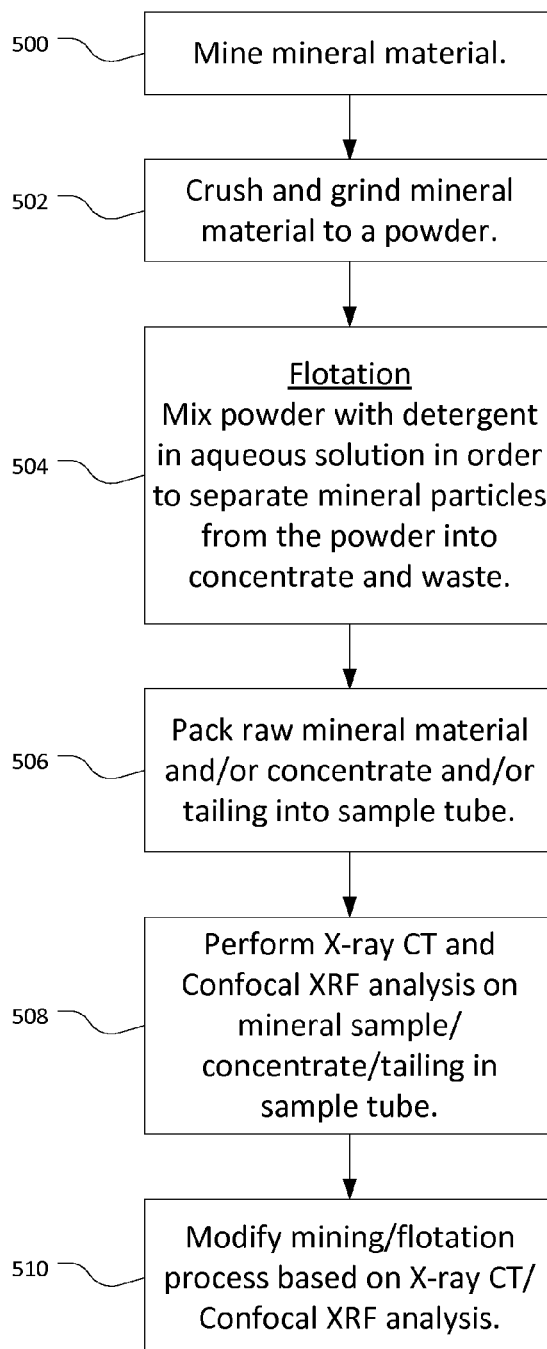


Fig. 10

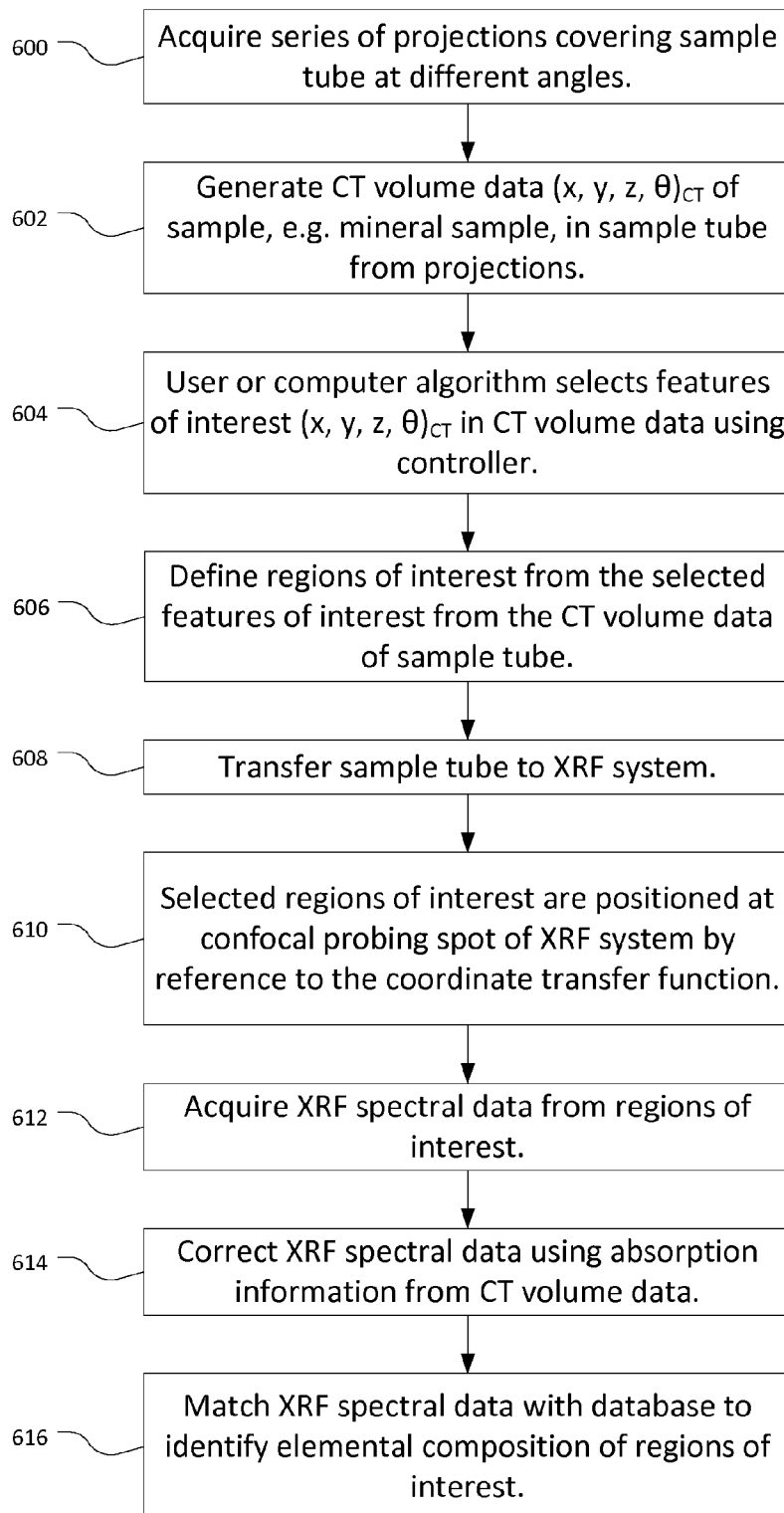
Analysis of sample using separate X-ray CT and XRF systems

Fig. 11A

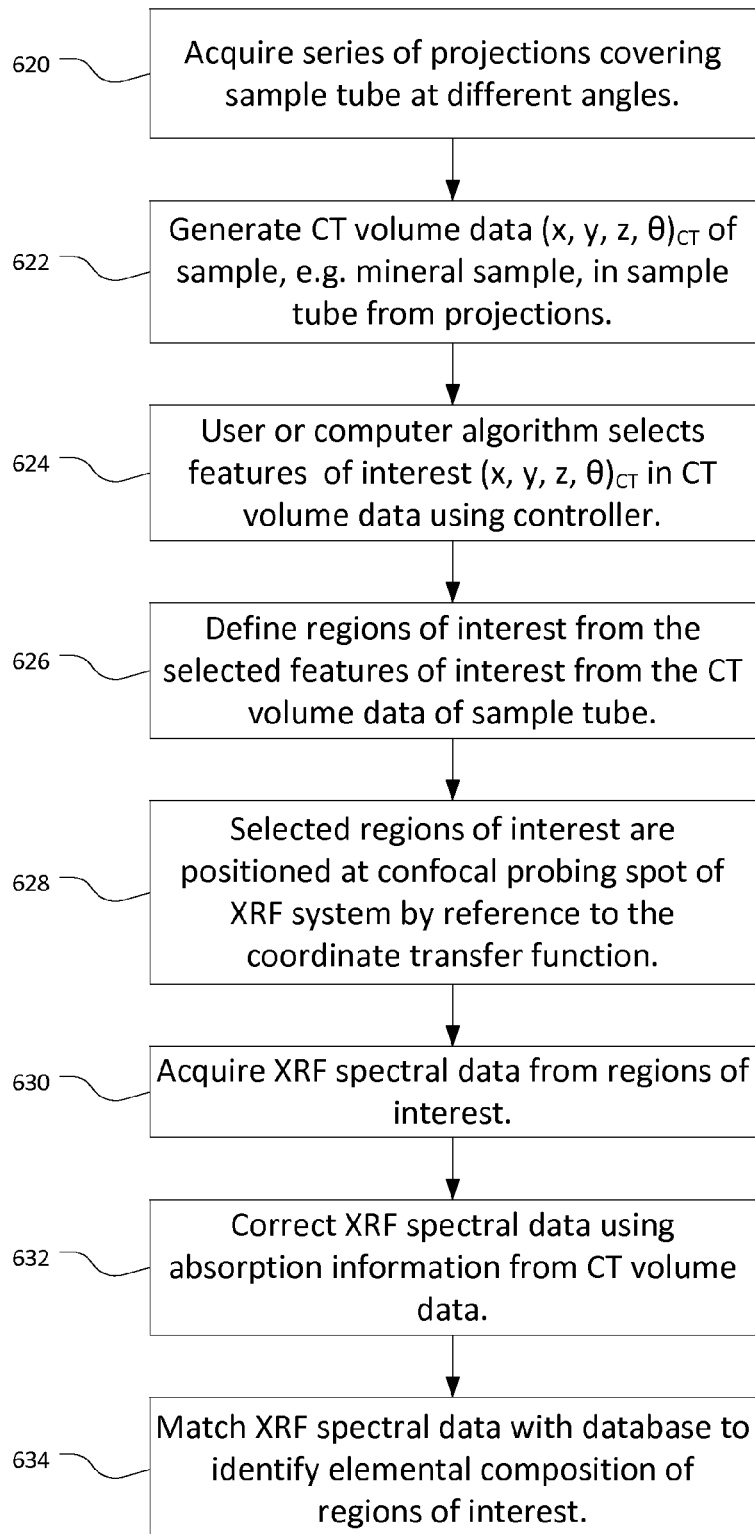
Analysis of sample using integrated X-ray CT/XRF system

Fig. 11B

Raster scan analysis of sample using separate X-ray CT and XRF systems

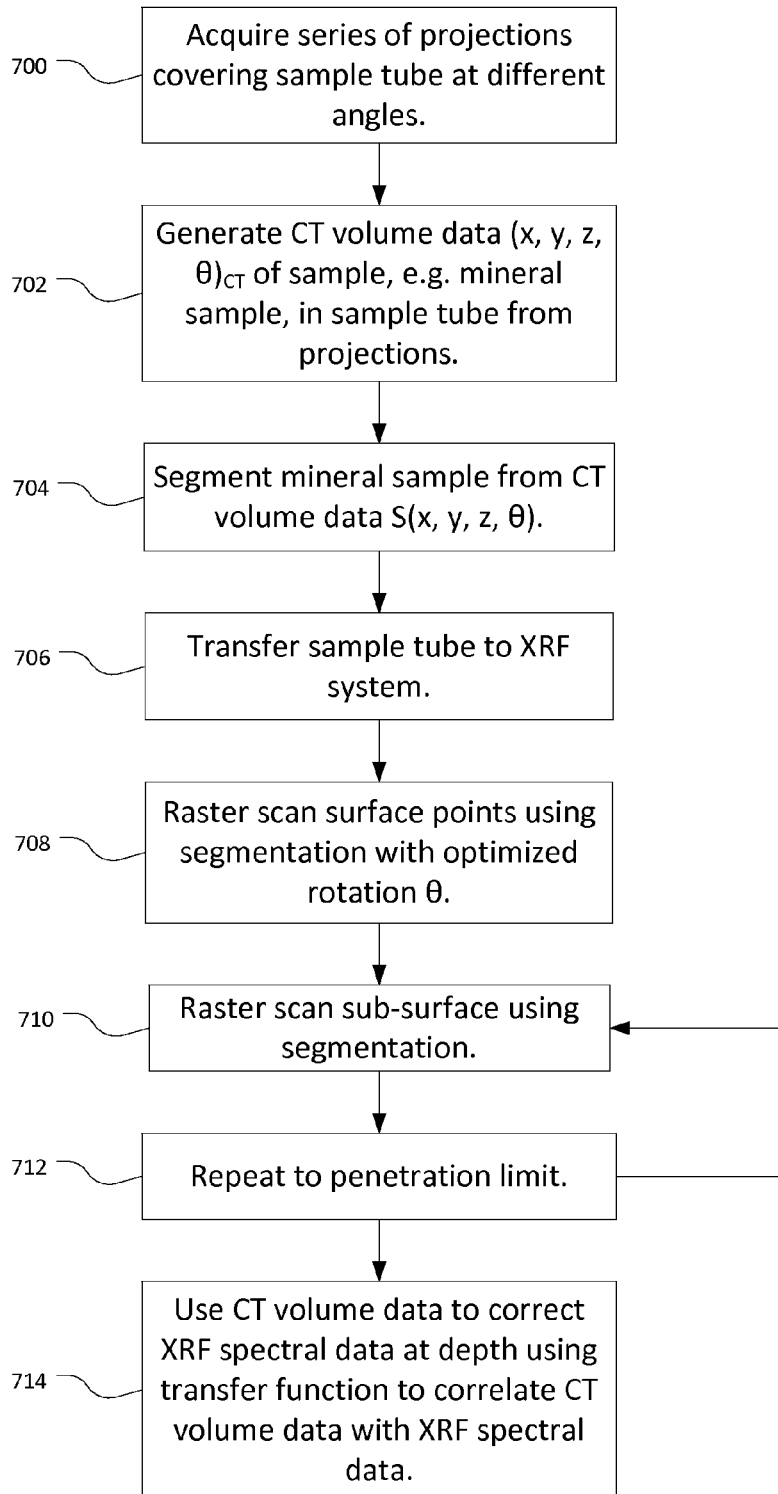


Fig. 12A

Raster scan analysis of sample using integrated X-ray CT/XRF system

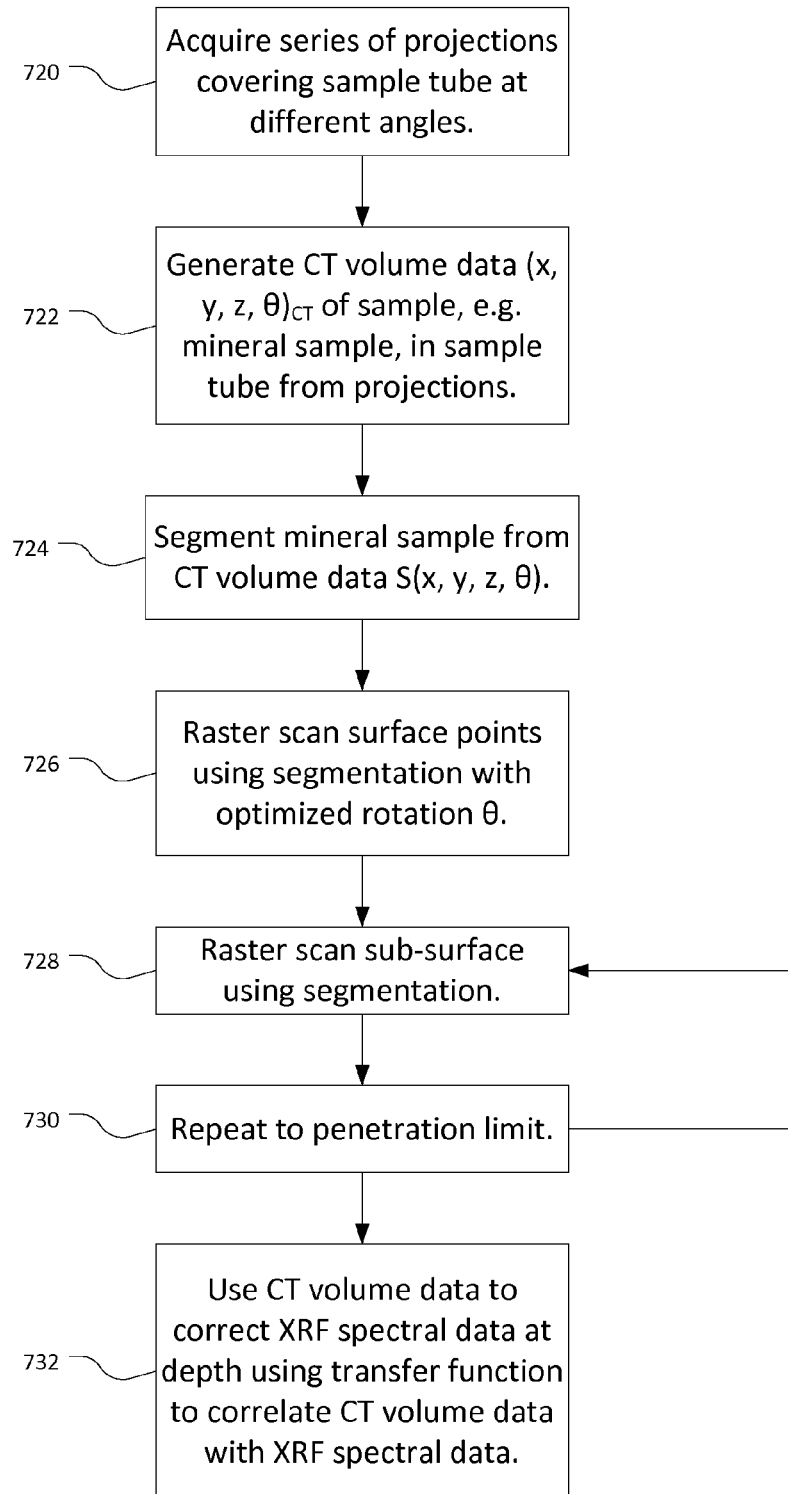


Fig. 12B

Determining the composition of sample using X-ray CT and  
XRF systems

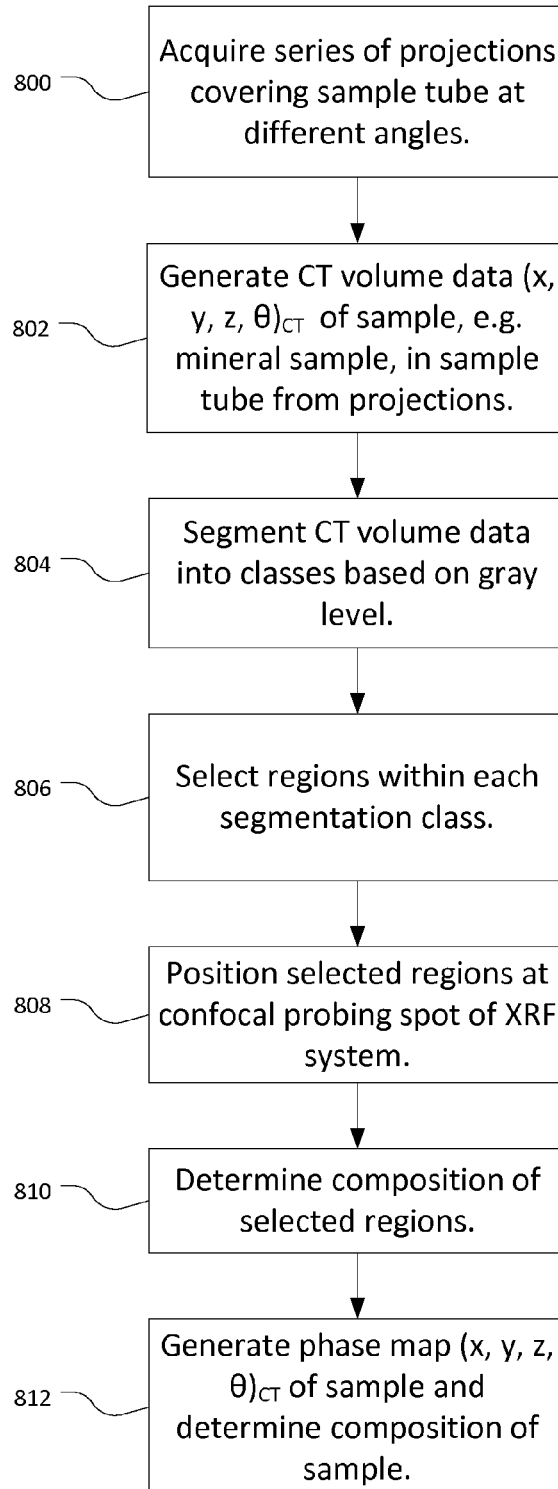


Fig. 13

1

**COMBINED CONFOCAL X-RAY  
FLUORESCENCE AND X-RAY  
COMPUTERISED TOMOGRAPHIC SYSTEM  
AND METHOD**

RELATED APPLICATIONS

This application is a §371 National Phase Application of International Application No. PCT/US2013/058464, filed on Sep. 6, 2013, now International Publication No. WO 2014/039793 A1, published on Mar. 13, 2014, which International Application claims the benefit under 35 U.S.C. §119(e) of U.S. Provisional Application No. 61/698,137, filed on Sep. 7, 2012, all of which are incorporated herein by reference in their entirety. This application is related to U.S. application Ser. No. 14/020,180, filed on Sep. 6, 2013, now U.S. Publication No. 2014/0072095 A1, published on Mar. 13, 2014.

BACKGROUND OF THE INVENTION

High-resolution x-ray computed tomography (CT) is a widespread imaging modality with many research and development, as well as industrial, applications. CT systems with three-dimensional (3-D) spatial resolution down to and exceeding one micrometer are available commercially. These systems are widely used for research and find increasing use in industrial applications. See [Scott\_2004]-Scott, David et al, A Novel X-ray Micro tomography System with High Resolution and Throughput For Non-Destructive 3D Imaging of Advanced Packages, ISTFA 2004: 30th International Symposium for Testing and Failure Analysis; Boston, Mass.; USA; 14-18 Nov. 2004, 94-98; and [Stock\_2008]-Stock, S. R, Recent advances in X-ray microtomography applied to materials, *Int. Mater Rev*, 1008, 53, 129-181.

X-ray CT scanning systems generate three-dimensional tomographic volumes of the samples from a series of projections at different angles. Projections are also referred to as 2-D projection images, or projection data. The tomographic volumes are generated from the projection data using software reconstruction algorithms based on back-projection and other image processing techniques to reveal and analyze features within the samples.

X-ray CT has a long track record in integrated circuit (IC) failure analysis. More recently, CT is being used in oil and gas rock analysis to determine porosity and model flow characteristics [Ingrain Digital Rock Physics]. This application has been added to its list of industrial applications. Currently, rapid adoption of high-resolution CT for mining applications is occurring starting with research institutions ([Miller\_2009]-Miller, J. D et. al, Liberation-limited grade/recovery curves from X-ray micro CT analysis of feed material for the evaluation of separation efficiency, *Int. J. Miner. Process*, 2009, 93, 48-53) and has found its way into industrial laboratories with initial focus on tailings analysis for floatation.

Tailings from mining operations are materials left over from processing after most of the valuable minerals have been extracted. Typically, the tailings particles are very small in size—the sizes are of the order of a micrometer to about 100 micrometers ( $\mu\text{m}$ ) or less for platinum and gold operations and can reach down to about a micrometer. Platinum bulk concentrations in tailings are only on the order of 0.5 parts per million (ppm) currently (compared to a few ppms for the raw ore). While the bulk concentrations are very small, the precious metals are not distributed uniformly in the tailings. In fact, they are found in micron

2

sized grains highly localized in space. Left over precious metal is not extracted due to its small particle size, inclusion or association with non-floating minerals, or other inefficiencies of the separation (floatation) process. However, the increasing energy and extraction costs as well as increasingly lower grade of raw ore have created large economic incentives for mining companies to characterize tailings samples better in order to recover precious metals more efficiently through the optimization of separation processes, for example.

Currently, the main scientific instrument used to characterize these tailings is the Mineral Liberation Analyzer (MLA). It is accepted as a standard for accurate mineralogy analysis. The MLA integrates a scanning electron microscope (SEM) with energy dispersive spectroscopy (EDS) having automated sample handling and analysis software dedicated for mineralogy applications.

For tailings analysis, the tailings particles are dispersed and fixed in epoxy such that they are physically separated from each other. These samples are then cut and polished for study under the SEM. First, a back scattered electron (BSE) image of the surface is acquired with high spatial resolution. The signal acquired in the BSE image is proportional to the density and atomic number of the minerals contained in these particles; and the images are depicted with different shades of grey. To accurately determine the mineral composition inside these particles, multiple EDS spectra are obtained and analyses of these spectra provide the basis for determination of minerals.

During the last 10 years, the analysis of tailings with MLA has been attributed with the increased efficiency of extraction of platinum from ore and has led to a decrease of platinum concentration in tailings from  $\sim 1$  ppm to 0.5 ppm.

SUMMARY OF THE INVENTION

However, the continued study of tailing samples using MLA has multiple problems, chief amongst them are:

1. Tailings from platinum extraction operations typically have the lowest number of particles that actually contain platinum, typically of the order of 0.5 ppm. Thus, multiple samples have to be measured to acquire statistically meaningful data. Often, up to 18 tailing samples (“pucks”), each about 30 millimeters (mm) in diameter, are studied at a time; and this generates only a low statistical data set generally not sufficient to conduct meaningful experimental studies to increase yield.
2. MLA is inherently a two-dimensional (2-D) method and hence only limited information is obtained. This is due to the fact that platinum that is slightly above or below the cut will not be resolved and the 3-D context of the particle remains undetermined. To determine the 3-D context in any statistically significant way, more than 50 cross sectional views of representative particles would typically have to be acquired, which increases the total time to results.
3. Traditional 2-D analysis from SEM has overestimated mineral recovery [Miller\_2009]. Only a complete 3-D analysis can provide an unambiguous solution to the grade recovery curve that is important for determining the operational efficiency of a mining operation.
4. Typical time to results with MLA can be up to 5 days due to the complexity of sample preparation and measurement.
5. The BSE image of the sample utilized for the MLA method is destructive in nature. To obtain information

about features of interest deeper within the sample, the operator has to physically grind and polish the sample down to the desired plane depth, destroying the sample in the process.

High resolution x-ray CT technology has the potential to overcome all of the problems inherent to MLA mentioned above. The CT technique enables the sampling of a relatively large 3-D volume in a matter of a few hours to locate minerals of interest, such as platinum grains. This enables collection of statistically relevant data with a very short turn-around time allowing for the design of experiments. With the unambiguous, isotropic information content of x-ray CT, true 3-D data of individual particles are collected to completely describe the liberation state of the platinum grains and grain association, which is important for understanding the root cause of yield.

Moreover, because x-ray CT technology provides non-destructive imaging of samples at arbitrary depth within the sample, operators can utilize the x-ray CT to generate projection images at different depths within the sample, and combine the images into a 3-D volume. The 3-D volume information generated is also known as a CT volume dataset.

Once the volume datasets have been generated, x-ray CT systems preferably enable the selection of two-dimensional, cross-sectional "slices" within the three-dimensional tomographic volume data sets via software tools. These tools typically allow an operator to select a synthetic or tomographic slice at an arbitrary angle within the volume datasets for analyzing information within the sample. This also provides the ability to locate features within the sample at an arbitrary depth, all while leaving the sample intact.

X-Ray Fluorescence (XRF) is a very popular and well-established characterization technique for determining the elemental composition of samples. An enhancement to standard XRF, called confocal XRF, typically utilizes two polycapillary focusing optics for providing enhanced XRF elemental analysis over standard XRF techniques.

Confocal XRF was conceived about 20 years ago [Kumakhov\_1996], but it is only over the past few years that many researchers at various synchrotron facilities have employed confocal set ups. The applications have ranged from elemental imaging in environmental chemistry ([De\_Samber\_2008]-De Samber, B et al, Three-dimensional elemental imaging by means of synchrotron radiation micro-XRF: developments and applications in environmental chemistry, *Anal Bioanal Chem*, 2008, 390, 267-271) to the study of composition and structure of ancient paintings ([Malzer\_2006]-Malzer, W, 3D Micro X-ray Fluorescence Analysis, *The Rigaku Journal*, 2006, 23, 40-47) as well as element to tissue correlation in biological samples ([De\_Samber\_2010]-De Samber, B et. al, Element-to-tissue correlation in biological samples determined by three-dimensional X-ray imaging methods, *J. Anal. At. Spectrom.*, 2010, 25, 544-553). Sensitive trace element detection of transition elements has also been demonstrated ([Janssens\_2003] Janssens, K et. al, Minimum Detectable Amounts and Minimum Detection Limits of Normal and Confocal  $\mu$ -XRF at Hasylab BL L, in pink beam mode, *HASYLAB Jahresbericht 2002/Schneider J. [edit.], e.a., Hamburg, 2003.*). Currently, with the state of the art technology for fabricating polycapillary optics, confocal volume of ( $\sim 20 \mu\text{m}$ )<sup>3</sup> has already been achieved.

Significant work has been performed in synchrotron facilities to quantify the minimum detection limits and minimum detection amounts of the confocal XRF technique [Janssens\_2003, De\_Samber\_2010]. [Janssens\_2003] work has reported sensitivity losses in the confocal setup due to

higher air absorption of softer fluorescence x-rays, but confocal XRF had significantly better peak to background ratios for bulk samples compared to conventional XRF, which enabled sub-ppm detection. Some groups have applied their laboratory based confocal XRF setup to probe and analyze paint layers [Wolzer\_2006]. They reported (10-100 times) worse detection limits than with synchrotron sources albeit with sub optimal setup.

High resolution 3-D x-ray CT has become a widespread imaging modality across many disciplines including materials science, biology, geology, and semiconductors, to name a few. The main shortcoming of x-ray CT is that it produces only "grey scale" images where the intensity of a feature in the image is a proxy for the local mass density (away from x-ray absorption edges).

Thus, in the present invention, x-ray CT is combined with confocal XRF to provide a more complete characterization and understanding of a sample. The detection of 3-D distribution of structures inside the sample is coupled with elemental composition analysis of those structures.

The capability of combining sub-micrometer spatial resolution 3-D imaging with elemental composition analysis in 3-D with ppm level sensitivity is important to many scientific research and industrial applications. A prime industrial example for this is the elemental identification of precious metal grains in crushed and ground ores and floatation tailings in the mining industry. This type of data enables better optimization of extraction yields and leads to improved financial and environmental benefits through the analysis of the 3-D liberation state of the micrometer-sized precious metal grains. The potential applications extend much farther, however. For example, in biological applications, toxicological effects can be related to tissue specific morphology and toxic trace element concentrations.

The present invention, in one example, includes integration of a confocal XRF system into an x-ray CT system as a correlative microscopy solution (CT/XRF). The CT/XRF system has an x-ray CT subsystem, or CT subsystem, and a Confocal XRF subsystem, or CXRF subsystem. When the CT subsystem is acquiring information from the sample, the CT/XRF system is said to be running in CT mode; when the CXRF subsystem is acquiring information from the sample, the CT/XRF system is said to be running in XRF mode.

After performing x-ray CT 3-D imaging of a sample into a CT volume dataset, the CXRF subsystem is preferably used to scan only a limited number of points or small areas predetermined from the structural information of the volume dataset. A controller of the CT/CXRF system manages the acquisition of volume information from the CT subsystem and the acquisition of elemental composition information from the CXRF subsystem.

This not only overcomes the lack of elemental contrast in CT-only systems, but the limited number of scan points targeted by the CXRF subsystem enables rapid scanning of the sample for determining its elemental composition. The scan points are efficiently selected to provide essential elemental composition information complementary to the CT volume dataset.

This overcomes the main challenge that confocal XRF systems have traditionally faced for widespread adoption, which is the prohibitively long scan times typically required for generating complete 3-D volumes. A key element of the CT/XRF system is exact correlation between the two modalities and the controller/control system that implements this functionality.

The CT/CXRF technology of the invention can deliver results similar to MLA. The data obtained by the invention

can be positively correlated with MLA results, using the elemental composition information that the invention provides for selected grains of interest within a sample. In addition, the ability of a combined CT/CXRF instrument to probe deeper layers within a sample provides a clear advantage over MLA, which is by nature a surface technology.

Moreover, the invention does not require the complex preparation of polished sections of the sample that is typical of MLA systems. The CT/CXRF technology of the invention provides non-destructive sample analysis.

Finally, the ability to identify and precisely locate features such as metal grains with respect to the boundary of the particles in 3D demonstrates superiority of this technique over MLA. Specifically, the system and method can provide for 3D contextual information that can be used to determine the liberation state of the elements of the grains. This greatly improves extraction yields over MLA, because the inherently 2D technique that MLA provides has been shown to overestimate the mineral recovery [Miller 2009].

In general, according to one aspect, the invention features an x-ray computed tomography (CT)/x-ray fluorescence (CXRF) system. This system comprises an x-ray CT subsystem for acquisition of volume information and a XRF subsystem, e.g., confocal, for acquisition of elemental composition information. A controller in communication with the x-ray CT subsystem and the XRF subsystem manages the acquisition by the x-ray CT subsystem and the XRF subsystem.

In one example, the controller provides spatial calibration of the confocal XRF subsystem based on the volume information received from the x-ray CT subsystem.

The controller combines the volume information from the x-ray CT subsystem with the elemental composition information from the XRF subsystem to verify a liberation state of elements within the sample. The controller selects a limited number of points or small areas predetermined from the volume information for the acquisition of the elemental composition information by the XRF subsystem.

In addition, the controller preferably performs correlation between the volume information and the elemental composition information to provide elemental contrast of the sample as a function of depth. In response to the correlation, the controller generates elemental distribution maps as a function of position within the sample.

In one example, the controller generates an interactive graphic, which enables the identification and selection of a feature of interest within the volume information acquired by the x-ray CT subsystem. The controller also defines a region of interest that includes the feature of interest. The region of interest is used to translate the feature of interest from x-ray CT subsystem coordinates to XRF subsystem coordinates. Finally, the controller accesses the region of interest with the XRF subsystem for the acquisition of the elemental composition information.

In the example, the controller generates a coordinate transfer function that translates between x-ray CT subsystem coordinates and confocal XRF subsystem coordinates. The controller generates the coordinate transfer function to account for differences in resolution, for example, between the x-ray CT subsystem and the confocal XRF subsystem. The controller generates the coordinate transfer function for translating selected features of interest from the volume information of the x-ray CT subsystem into a region of interest for acquisition of the elemental composition information by the XRF subsystem.

The XRF subsystem positions the region of interest at a confocal probing spot of the XRF subsystem by referencing

the coordinate transfer function. The controller corrects the elemental composition information acquired by the confocal XRF subsystem using absorption information of the volume information acquired by the x-ray CT subsystem. The absorption information is associated with voxel intensities of the volume information.

The controller can compare the elemental composition information acquired by the confocal XRF subsystem against reference elemental information to identify elements in the sample. The reference elemental information is typically included within a database that communicates with the controller. The XRF subsystem selectively probes a region of interest of the volume information at a sub-micrometer spatial resolution for the acquisition of the elemental composition information.

In general, according to another aspect, the invention features a method for analyzing a sample using x-ray computed tomography and x-ray fluorescence. The method comprises preparing a sample, obtaining a three-dimensional x-ray computed tomography (CT) measurement of the sample, selecting of features of interest in the CT measurement of the sample, defining regions of interest from the selected features of interest, acquiring x-ray fluorescence (XRF) spectra from the defined regions of interest, and matching the acquired XRF spectra with reference elemental information for identification of elements within the sample.

The above and other features of the invention including various novel details of construction and combinations of parts, and other advantages, will now be more particularly described with reference to the accompanying drawings and pointed out in the claims. It will be understood that the particular method and device embodying the invention are shown by way of illustration and not as a limitation of the invention. The principles and features of this invention may be employed in various and numerous embodiments without departing from the scope of the invention.

#### BRIEF DESCRIPTION OF THE DRAWINGS

In the accompanying drawings, reference characters refer to the same or similar parts throughout the different views. The drawings are not necessarily to scale; emphasis has instead been placed upon illustrating the principles of the invention. Of the drawings:

FIG. 1A is a perspective schematic view of an integrated x-ray CT/XRF system in CT mode according to an embodiment of the invention.

FIG. 1B is a perspective schematic view of the integrated x-ray CT/XRF system from FIG. 1A in XRF mode.

FIG. 2 is a perspective schematic view of an x-ray CT/XRF system including a separate x-ray CT subsystem and a separate confocal XRF subsystem that function together according to another embodiment of the invention.

FIG. 3 is a top schematic view of an integrated x-ray CT/XRF system running both the CT mode and the XRF mode simultaneously or serially according to another embodiment of the invention.

FIG. 4 is an exemplary interactive graphic provided by a controller of the x-ray CT/XRF system for a tailings sample, where the interactive graphic enables operator selection of a feature of interest within a slice selection of the CT volume dataset of the sample;

FIG. 5 shows the XRF spectral data obtained by the CXRF subsystem for the region of interest in FIG. 4;

FIGS. 6A-6D shows a workflow that illustrates the correlative aspects of the invention, for a feature of interest selected by an operator within a representative tailings sample;

FIG. 7 is a plot of x-ray photon counts as a function of energy (keV) showing the XRF spectral data for a tailings sample that includes Platinum (Pt), for illustrating the sensitivity of the x-ray CT/XRF system;

FIG. 8 is a schematic block diagram of a controller showing its interaction between the x-ray CT subsystem and the CXRF subsystem;

FIG. 9 is a flowchart illustrating an x-ray CT/XRF system calibration method according to an embodiment of the invention;

FIG. 10 is a flowchart illustrating a method for acquiring and preparing a mineral material for x-ray CT/XRF analysis according to an embodiment of the invention;

FIG. 11A is a flowchart illustrating a method of analyzing a sample using separate x-ray CT and Confocal XRF subsystems according to an embodiment of the invention;

FIG. 11B is a flowchart illustrating a method of analyzing a sample using an integrated x-ray CT/XRF system according to an embodiment of the invention;

FIG. 12A is a flowchart illustrating a raster scan analysis of a sample using separate x-ray CT and Confocal XRF subsystems according to an embodiment of the invention;

FIG. 12B is a flowchart illustrating a raster scan analysis of a sample using an integrated x-ray CT/XRF system according to an embodiment of the invention; and

FIG. 13 is a flowchart illustrating a method of determining the composition of a sample using an x-ray CT/XRF system according to an embodiment of the invention.

#### DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

3-D images delivered by x-ray CT include a cubic array of voxels with "average" attenuation values. These values are represented by "grey levels". The differences in grey levels, or voxel intensities, correspond to differences in attenuation and are representative of the material that caused this attenuation. A histogram of these grey level values allows one to analyze and determine the various materials and their phases present in the image, provided the grey levels are suitably calibrated. These grey levels are often sufficient for many applications such as IC failure analysis or porosity analysis for oil and gas rock analysis.

For tailings analysis in mining, ambiguities arise due to so-called grey-scale overlaps. These occur if materials with different elemental composition exhibit very similar or same grey levels in the x-ray CT data. For example, if a small high-density grain is found in a tailings sample, it is generally not possible to positively identify this grain as a platinum compound compared to some other high-density compounds (e.g. lead, palladium, etc.). Several hundred known platinum compounds can be present with varying density (and grey scale values) in addition to countless other high-density compounds composed of other elements, making elemental identification extremely important.

The system and method here enables the probing of a grain for elemental composition analysis to give a positive identification to the element and further enables the narrowing of the precise compound. Additionally, in biological applications, the availability of trace-element sensitive spatially resolved probing is useful for toxicological studies to directly put structural changes in context with the presence of toxins.

One of the proposed solutions to some of the problems with the current technology is to complement the x-ray CT scanner with a confocal XRF setup that is able to selectively probe points or small volumes of the x-ray CT volume at a spatial resolution of less than  $\sim(100 \text{ }\mu\text{m})^3$  and preferably less than  $\sim(50 \text{ }\mu\text{m})^3$ , and in some cases less than  $\sim(20 \text{ }\mu\text{m})^3$  with ppm level sensitivity.

The ppm sensitivity on bulk homogeneous samples is achieved with confocal XRF. For highly complex and heterogeneous samples as well as samples with very small bulk concentrations where elements to be detected are highly concentrated in very small volumes and localized in space (such as in tailings samples in mining industry), confocal XRF has significant advantages over conventional XRF due to its ability to define the volume of interest to be probed. Confocal XRF also allows for significantly improved signal to background ratios to efficiently detect localized concentrations of elements in thick samples.

One of the chief reasons why the confocal XRF technique has not been commercialized is the non-practicality of scanning large volumes in a reasonable time. Although each point takes only a very short measurement time, usually measured in seconds, a small volume ( $50 \times 50 \times 50$  pixels) can lead to exorbitant measurement times (173 hours for example for a point dwell time of 5 seconds). The key to make confocal XRF practical is to combine it with x-ray CT and only probe a limited number of points in the 3-D volume that are relevant.

This is achieved with the combined CT/XRF system by performing an x-ray CT scan first and then selecting, based on the 3-D structural information, where to collect the elemental information data. As noted earlier, the very small concentrations of platinum are found in micron sized grains highly localized in space and for tailing samples measured in the mining industry only a small number (sometimes as low as  $\sim 10$ ) of grains per x-ray CT scan will be of interest for elemental identification. Such geometry lends itself naturally for the confocal XRF technique and these can be measured by confocal XRF within minutes, adding only minimal time to the CT scan times. This is due to the fact that the grains containing platinum have volumes of the order of  $(2 \text{ }\mu\text{m})^3$  inside the confocal volumes of the order of  $(20 \text{ }\mu\text{m})^3$  or about 1000 ppm by volume. This leads to very efficient detection of precious metals which is not possible with conventional XRF.

The same argument holds true for other key applications requiring elemental identification, such as CT grey scale calibration, which generally requires probing only a very limited number of data points in order to correlate grey levels with elemental make-up. For biological applications, it is generally sufficient to probe only within the tissue of the same kind to get a representative level of trace elements. For example, in a Zebra fish sample, one would perform measurements within the organs (or a few points within each organ) and not attempt to point-scan the whole specimen.

The coupling of high resolution x-ray CT with confocal XRF helps mitigate and overcome the inherent limitations of the confocal XRF technique on sample sizes. In particular, the coupling overcomes such limitations as limited x-ray penetration into samples and absorption of emergent fluorescence x-rays in the sample. This is because for high resolution x-ray tomography, sample sizes are typically of the order of 1-2 mm. For optimal excitation of platinum (and other precious metals) L fluorescence lines, Mo and Ag sources are, in some embodiments, used with polycapillary optics optimized for  $\text{MoK}\alpha$  ( $\sim 17.5$  kilo electron volts (KeV)) and  $\text{AgK}\alpha$  ( $\sim 22.2$  KeV) radiation, for which the

penetration depths inside tailings samples are of the order of ~2 millimeters (mm). For platinum  $L\alpha$  lines (~9.4 KeV) about 10% transmission is expected over ~1 mm which corresponds to a total sample thickness that can be used of ~2 mm (penetration of L x-rays are even larger). Higher transmission is expected for other L lines such as  $L\beta$  and  $L\gamma$  x-ray lines. For biological applications (for example, tissues), greater x-ray penetration depths (and consequently deeper probing) is achieved, which allows for larger samples to be used. For CT grey scale calibration, exhaustive probing of points deep inside the sample is usually not required. Instead, limited probing of selected points at or near the surface of the specimen is typically sufficient.

FIG. 1A shows an example of the integrated x-ray CT/XRF system **10** in CT mode, which has been constructed according to the principles of the present invention.

This integrated system **10** includes an x-ray CT subsystem **100**, or CT subsystem, and a confocal x-ray fluorescence subsystem **102**, or CXRF subsystem.

The integrated system **10** also includes a controller **128** that manages various parts of the x-ray CT subsystem **100** and the confocal x-ray fluorescence subsystem **102**. The controller **128** receives data from these subsystems **100/102**. Based on the data received, the controller **128** manages how these subsystems **100/102** operate accordingly and their operations coordinated.

The controller **128** also includes an interactive graphic **170**. The interactive graphic **170** provides interactive operator selection of features of interest **120** from the acquired volume information **150** of the sample **104**, and presents the selection and display via display device **136**. More detail on the controller **128** and its other components accompanies the descriptions for FIG. 4 and FIG. 8, herein below. These subsystems **100/102** are used together to determine the mineral content of a sample **104**. Examples of samples **104** include mineral samples such as sandstone, bituminous sand, ore, and coal or samples containing precious metals or fluids, such as water or crude oil.

In the illustrated example, the sample **104** is held within a sample tube **110**. This sample tube **110** is a glass or plastic test tube, for example. In one example, the size of the sample is about 1-4 mm in diameter and ~2-20 mm in height.

In another example, the sample is a flat sample that is placed, or in a sample container other than the sample tube. Alternatively, the sample has a different configuration such as cubic or spherical. When flat samples are used, x, y, z sample stage **112** has the capability to position different regions of the flat face of the samples in the x-ray beams.

The sample tube **110** is mounted on an x, y, z sample stage **112** that allows for the positioning of the sample **104** in the beam **107** generated by the x-ray source **106**. In one example, the x, y, z sample stage **112** comprises three orthogonal motorized positioning arms that allow for the positioning of the sample **104** along each of the three orthogonal dimensions under the control of the controller **128**.

The x, y, z sample stage **112** has an integrated rotation stage **114** preferably attached underneath the x, y, z sample stage **112**. The integrated rotation stage **114** enables the x, y, z sample stage **112** to rotate through 360 degrees around the vertical (z) axis. This allows the x, y, z sample stage to be rotated along with the sample tube **110** and sample **104** to any desired angle ( $\theta$ ) with respect to the x-ray CT subsystem **100** and/or confocal x-ray fluorescence subsystem **102**.

The rotation stage **114** is preferably a precision rotary stage such as an air bearing stage or a mechanical ball-bearing or roller bearing stage.

The x-ray CT subsystem **100** includes an x-ray source **106** that generates the x-ray radiation beam **107**. The x-ray source **106** is preferably a laboratory based source such as a sealed tube, rotating-anode, or micro-focus x-ray source. In one example, the x-ray source is a transmission x-ray micro-focus source with a source size of about 2  $\mu\text{m}$  or less operated up to a maximum power of 10 Watts. The small spot size or source size allows for high resolution imaging. Use of a transmission source allows for a favorable imaging geometry by shortening the distance between the source and a detector enabling high throughput.

When the sample **104** is a mineral sample, a high-energy x-ray radiation beam is selected with energy above several keV for the x-ray source **106**. This is typically required to penetrate samples with tens of micrometers or greater thickness. Higher energy radiation of tens of keV is used when the sample is usually about a millimeter or greater in thickness. Generally, the range is 5-150 keV. In one embodiment, the x-ray source has a tungsten target.

The x-ray CT subsystem **100** also includes a spatially resolved transmission detector **108**. In one example, the detector **108** is a scintillated CCD detector with optical magnification as described in U.S. Pat. No. 7,057,187 B1, which is incorporated herein by this reference in its entirety.

Specifically, the spatially resolved detector **108** records x-ray radiation **107** that passes through the sample **104**. In one example, the spatially resolved detector **108** includes a scintillator, a charge-coupled device (CCD) camera, and a lens or lens system for imaging visible light from the scintillator onto the CCD camera.

In CT mode, the x-ray CT subsystem **100** performs sub-micrometer spatial resolution 3-D imaging of the sample **104**. The x-ray source **106** emits x-rays **107** that penetrate the sample **104**. Then, the x-rays **107** are detected and recorded by the spatially resolved detector **108**.

The generated images are passed from the spatially resolved detector **108** to the controller **128**. The controller **128** operates the x-ray source **106** and the spatially resolved detector **108** to generate a series of projections **156** of the sample **104**. The controller **128** also operates the rotation stage **114**. In between projections **156**, the controller **128** advances the rotation stage **114** through a predetermined arc. Once enough projections **156** have been generated at different values for  $\theta$ , the controller **128** combines the images or projections **156** into a 3-D tomographic image of the sample **104**. In one embodiment, the sample is rotated through 360 degrees during the scan. In another embodiment, the angular range for scanning the sample is limited to 180 degrees or lower.

In one example, a series of 2D projection images **156** (typically about 1600 images or more) are obtained and mathematically reconstructed to produce a 3-D volume, with grey value in each voxel representing the optical density. The conditions of acquisition of images are optimized for speed and maximization of signal to noise ratios.

Source filters **157** are used in some examples, to pre-harden the beam **107** incident on the sample **104** to ensure proper beam hardening corrections to the reconstructed data. Suitable calibration can be performed and CT numbers obtained in terms of Hounsfield Units which gives a measure of linear attenuation coefficient in the material at a given location.

In one embodiment, the controller **128** commands the switching of the x-ray source **106** from CT mode to XRF mode and back to CT mode. This can be accomplished with a switchable source optical element **116** such as an elliptical polycapillary optic. In one example, the switchable source

## 11

optical element 116 is attached to the x-ray source 106 via a moveable arm 118. When the controller 128 directs the x-ray source 106 to switch to XRF mode, the switchable source optical element 116 is positioned into the path of the x-rays 107 and in front of the x-ray source 106 as shown in FIG. 1B. When the controller 128 directs the x-ray source 106 to switch back to CT mode, the switchable source optical element 116 detaches from the x-ray source 106 and is moved out of the path of the x-rays 107 as shown in FIG. 1A.

FIG. 1B shows an example of the integrated x-ray CT/XRF system 10 in XRF mode.

During XRF mode, the source optical element 116 functions to control and direct x rays over a broad range of angles and energies from the source to generate a small focused beam 109 onto a volume or region of interest 122 in the sample 104.

The confocal x-ray fluorescence subsystem 102 further includes a collection optical element 124 and an x-ray fluorescence detector 126.

The collection optical element 124 is preferably a half optic that can be used to minimize the total number of reflections of x-rays inside the optical element 124. In another example, the collection optical element 124 is an elliptical polycapillary optic. The collection optical element 124 gathers fluorescence x-rays 111 that are generated within the particular region of interest 122.

The intersection of the foci of source optical element 116 and the collection optical element 124 defines the confocal volume which depends on the focus size and strongly depends upon the detected fluorescence x-ray energy. The confocal volume, as defined by the intersection of the foci of source optical polycapillary element 116 and the collection optical polycapillary element 124, is approximately  $(50 \mu\text{m})^3$  in one example or  $(20 \mu\text{m})^3$ , or less, in another example. In a current embodiment, the source optical element 116 is optimized for  $\text{AgK}\alpha$  (~22.2 KeV) characteristic x-rays from the source 106. On the detection side, the half optic collection optical element 124 is used to minimize the total number of reflections of x-rays inside the capillaries and increase efficiency of detection of fluorescence x-rays from the sample.

In general, the collection optical element 124 is optimized to detect fluorescence x-rays in the energy range of 9-13 KeV (suitable for detection of precious metals) most efficiently. For examples where mid Z transition elements have to be efficiently detected, the collection optical element 124 is suitably optimized for the K lines of these elements whose energies lie in the 7-10 KeV range. The length of the collection optical element 124 is optimized and the distance between the energy dispersive detector 126 and the sample surface is minimized to reduce the absorption of softer fluorescence x-rays in air such that the sensitivity of the instrument is not severely compromised.

The collection optical element 124 produces or collimates a parallel beam of fluorescence x-rays 113 onto the x-ray fluorescence detector 126. The x-ray fluorescence detector 126 is an energy-dispersive x-ray spectroscopy (EDS) detector, in one example. The EDS detector converts the x-ray energy received from the collimated fluorescence x-rays 113 into voltage signals. Based on the voltage signals (characterizing x-ray energy), elemental composition information 152 of the region of interest 122 is determined.

The controller accepts the elemental composition information 152, also known as an XRF spectral dataset 152, from the CXRF subsystem 102. The XRF spectral dataset

## 12

152 acquired by the CXRF subsystem 102 includes individual characteristic peaks 166 associated with individual elements.

In examples, XRF spectral datasets 152 for regions of interest 122 include characteristic peaks 166 associated with different elements, such as the FIG. 7  $\text{L}\alpha$  line 162 and the FIG. 7  $\text{L}\beta$  line 164 of platinum (9.45 KeV and 11.2 KeV), and the FIG. 5 characteristic peaks 166 of lead (10.45 KeV and 12.62 KeV) and Copper (Cu). The characteristic peaks 166 identify and distinguish between the elements in the sample 104.

The controller 128 is in communication with the confocal x-ray fluorescence subsystem 102. Based on the results of the CT analysis in FIG. 1A, the controller 128 selects subsequent regions of interest 122 from the volume information 150 to be probed by the x-ray fluorescence subsystem 102. In more detail, the controller 128 operates the x, y, z sample stage 112/rotation stage 114 to rotate around the z-axis and position the sample tube 110 along the x, y, and z axes in relation to the confocal x-ray fluorescence subsystem 102. This provides desired positioning of the region of interest 122 with respect to the x-ray source 106 and the collection optical element 124/x-ray fluorescence detector 126. The rotation/positioning is optimized to reduce absorption of fluorescent x-rays.

In XRF mode, the confocal x-ray fluorescence subsystem 102 performs elemental composition analysis of the sample 104. The x-ray source 106 emits x-rays through the switchable source optical element 116 which focuses or directs the x-rays 109 towards an analysis region or a region of interest 122 in the sample 104. Typically, the x-rays used for CT mode will not be optimal for the XRF mode. Thus, in one example, the source 106 uses a new Ag target that can be operated at greater than the energy used in CT mode, such as greater than 20 Watts or up to 50 Watts or more.

In general, in this and the subsequent embodiments, the CT imaging subsystem 100 typically uses an x-ray source with a high Z target such as tungsten target. However, for specialized CT applications other targets may be used such as Mo, Rh, Ag etc. The x-ray source produces a broad spectrum of x-rays with energies up to the maximum applied voltage chosen by the user. Any or all of the spectrum may be utilized for CT imaging. In contrast, the XRF subsystem 102 typically uses lower Z x-ray source targets such as molybdenum, rhodium, and silver that produce characteristic x-rays and continuum in the energy range most suitable to excite elements useful for precious metal mining analysis. Other lower Z targets such as Cu, Ni, Fe can also be used for XRF subsystem. If need be, even high Z targets containing W and Pt may also be used. The choice of targets depends specifically upon the application.

The focused x-rays 109 induce fluorescence of elements within the analysis region 122, which are collected by the collection optical element 124. The collection optical element 124 receives emitted fluorescence x-rays 111. Then, the collection optical element 124 collimates the x-rays 113 towards an x-ray fluorescence detector 126 for detecting the fluorescence x-rays 111/113 from the region of interest 122.

The controller 128 receives data regarding elemental composition information 152 of the region of interest 122 from the x-ray fluorescence detector 126 in the form of energy spectra. These data are converted by the controller 128 into their final form, XRF spectral data 152, that provide a map of the elemental composition of the sample 104 for each of the regions of interest 122 that is analyzed.

In FIG. 2, the CT/XRF system 10 is shown as two separate subsystems. CT mode or function is performed

using an x-ray CT subsystem **100**. Then, the sample tube **110** is transferred to a separate confocal XRF subsystem **102**. These separate subsystems are used in combination to determine the mineral content, for example, of the sample **104** within the sample tube **110**.

This CT/XRF system **10** includes a controller **128** that manages various parts of the x-ray CT subsystem **100** and the confocal x-ray fluorescence (CXRF) subsystem **102**. The controller **128** receives data from these subsystems **100/102**. Based on the data received, the controller manages how these subsystems **100/102** operate.

Typically, the sample tube **110** is first mounted on an x, y, z sample stage **112A** of the x-ray CT subsystem **100**. As described above, this x, y, z sample stage **112A** has an integrated rotation stage **114A** for rotating the sample tube **110** to any desired angle ( $\theta$ ) with respect to the x-ray CT subsystem **100**. The x-ray CT subsystem **100** includes a first x-ray source **106A** and a spatially resolved transmission detector **108**.

During CT mode, the CT subsystem **100** is activated to collect a series of projections **156** at different values for  $\theta$ . The projections **156** are combined into a 3-D tomographic reconstruction **150** of the sample **104**.

Specifically, the first x-ray source **106A** emits diverging x-rays **107** through the features of interest **120**. In one example, the x-ray source **106A** is a transmission x-ray micro source with source size of about  $2\ \mu\text{m}$  or less and preferably  $1.5\ \mu\text{m}$  or less operated up to a maximum power of 10 Watts. In another example, the x-ray source **106A** is a reflection source having a source size or spot size of about  $5\ \mu\text{m}$  or less operated at a power between about 10 and 30 Watts. These x-rays **107** are captured and recorded by the spatially resolved detector **108**. The spatially resolved detector **108** generates images from the detection of these x-rays **107**. These images are passed to the controller **128** to develop 3-D tomographic images **150** of the sample **104**. As described previously, the controller **128** operates the x-ray source **106A** along with the integrated rotation stage **114A** to obtain the projections **156** for the different values of  $\theta$ .

Next, the CT/XRF system **10** switches from CT mode to XRF mode. The sample **104** is switched from the x, y, z sample stage **112A** of the CT system **100** to the x, y, z sample stage **112B** of the XRF system **102**. A compatible kinematic mounting system is used for both systems **100, 102** to enable reproducible sample transfer that keeps a fixed coordinate transformation between both systems. In other examples, a reference marker that can be identified by both systems is used to enable the transfer of the coordinate system between both systems.

During the switch, the controller **128** provides spatial calibration of the confocal XRF subsystem **102** based on the results of CT mode. Spatial calibration is the transfer of system coordinates (x, y, z,  $\theta$ ) from the x-ray CT subsystem **100** to the confocal x-ray fluorescence subsystem **102**. The controller **128** receives CT system coordinates **204** (x, y, z,  $\theta$ )<sub>CT</sub> from the x-ray CT subsystem **100** that characterize the locations of the features of interest **120**. The CT system coordinates **204** (x, y, z,  $\theta$ )<sub>CT</sub> are converted by the controller **128** to XRF system coordinates **207** (x, y, z,  $\theta$ )<sub>XRF</sub>. This conversion defines a region of interest **122** for the confocal XRF subsystem **102**.

The confocal XRF subsystem **102** includes a second x-ray source **106B** in communication with the controller **128**. The controller **128** adjusts this second x-ray source **106B** accordingly during XRF mode. In one example, the second x-ray source **106B** is a laboratory micro focus source with Ag target that is operated at greater than 20 Watts or 50 Watts

or more. Generally, however, the source's target as a Z of less than 50, as discussed previously.

The confocal XRF subsystem **102** also has a second rotation stage **114B** and a second x, y, z sample stage **112B** for receiving and holding the sample tube **110** from the x-ray CT subsystem **100**. The controller **128** directs the rotation of the sample tube **110** via the second x, y, z sample stage **112B/rotation stage 114B** based on the XRF system coordinates **207**.

The confocal XRF subsystem **102** includes the source optical element **116** such as an elliptical polycapillary optic for focusing the x-rays **109**. The source optical element **116** can be attached to the second x-ray source **106B** or placed in front of the second x-ray source **106B**.

The confocal XRF subsystem **102** is able to collect fluorescence radiation with the collection optical element **124** and detect that radiation with the x-ray fluorescence detector **126** as described above.

In XRF mode, the separate confocal x-ray fluorescence subsystem **102** performs elemental composition analysis of the sample **104**, which is typically limited to regions of interest **122** identified in the CT analysis. The second x-ray source **106B** emits x-rays **107** through the source optical element **116** which focuses the x-rays **109** towards a region of interest **122** in the sample **104**. In the illustrated example, the controller operates the rotation stage **114B** and the x, y, z sample stage **112B** of the XRF subsystem **102** to place the desired regions of interest **122** at the focal point of the source optical element **116** and the collection optical element **124**. The focused x-rays **109** induce fluorescence of elements within the region of interest **122**. Fluorescence x-rays **111** are received and guided by the collection optical element **124** towards an x-ray fluorescence detector **126** for detecting the fluorescence x-rays **111/113** from the region or volume of interest **122**.

The controller **128** receives data regarding energy of the x-rays detected by the fluorescence detector **126** and thus the elemental composition information **152** of the region of interest **122**. The XRF spectral datasets **152** provide a map of the elemental composition of the sample for the analyzed regions of interest **122**. After performing correction of the XRF spectral **152** using depth information of the volume information, the controller matches the XRF spectral datasets **152** to reference elemental information **168**.

Using the reference elemental information **168**, the controller converts the XRF spectral data into element-specific estimates of concentrations present in the sample, identifying characteristic peaks **166** of the XRF spectral datasets **152**. The controller **128** then displays the XRF spectral datasets **152** onto display device **136**.

In addition, the controller correlates information from the CT volume dataset/volume information **150** and the elemental composition information/XRF spectral datasets **152** for the region of interest **122**. More detail for the correlation capability of the controller **128** accompanies the description for FIG. 6A-6D and FIG. 8.

FIG. 3 illustrates another example of a CT/XRF system **10**. This is a top view of an integrated CT/XRF system **10** that has the capability of running both CT analysis and XRF analysis simultaneously or sequentially without removing the sample from the system.

In this example, two x-ray sources **106A/106B** are used. The first x-ray source **106A** is for CT analysis. The second x-ray source **106B** includes an optical element **116** attachment for XRF analysis.

In simultaneous CT/XRF mode, the first x-ray source **106A** emits a dispersive group of x-rays **107** across features

## 15

of interest **120** in the sample **104**. The second x-ray source **106B** utilizes the source optical element **116** to emit a focused set of x-rays **109** at a region of interest **122** in the sample **104**.

The CT/XRF system **10** can simultaneously develop 3-D CT images as well as XRF elemental composition images during CT/XRF mode. The x-rays **107** are captured and detected by the spatially resolved detector **108**. The focused x-rays **109** are collected and guided by the collection optical element **124**. The collection optical element **124** captures the fluorescence x-rays **111** and directs the rays **113** as a parallel beam towards an x-ray fluorescence detector **126** for detecting the fluorescence rays **111/113** from the region of interest **122**.

The CT/XRF system **10** can alternatively run CT mode or XRF mode at different times from one another. For example, the CT/XRF system **10** is run in CT mode first to determine desired features of interest **120** in the sample **104**. Then, the system **10** is run in XRF mode to analyze the regions of interest **122** that surround the desired features of interest **120** to thereby determine the elemental composition.

FIG. **4** displays an exemplary interactive graphic **170** generated by the controller **128**, for a representative tailings sample **104**. Preferably, the interactive graphic **170** displays volume information **150** generated by the x-ray CT subsystem **100** from the projections for the sample **104**. Using a slice selector **140**, the operator selects a synthetic slice **142** within the volume information **150**, and the interactive graphic **170** displays a 2-D image of the slice **142** in response to the selection.

The synthetic slice **142** includes clusters **144** of pixels associated with grains of elements and compounds of the sample **104**. In tailings samples, the clusters **144** typically include trace metals such as Iron (Fe), Platinum (Pt), Copper (Cu), and Chromium (Cr).

The gray levels of pixels in a slice **142**, or voxels within the full CT volume dataset **150**, correspond to attenuation of x-rays for features within the sample **104** in response to the CT scan. The brightness of the gray levels for each pixel/voxel reflect the proportion of X-rays scattered or absorbed as they pass through the sample. The brightest clusters **144** correspond to metallic elements and compounds, which typically absorb the highest proportion of incident x-rays within a sample **104**.

Within the selected slice **142**, the operator then selects a feature of interest **120**, such as one of the brighter clusters **144** associated with metallic elements and compounds. The controller **128** then calculates a region of interest **122** that surrounds the feature of interest **120**. The controller provides the region of interest **122** to the CXRF subsystem **102** to use as an acquisition target for performing elemental compositional analysis. More detail and supporting information for the creation of the region of interest **122** by the controller **128** accompanies the description for FIG. **8** in this section.

FIG. **5** shows an XRF spectral dataset **152** for the slice **142** and region of interest **122** selected in FIG. **4**. The XRF spectral dataset **152** has been compared to reference elemental information **168**. In one example, the reference elemental information **168** is included in a database **154** that communicates with the controller **128**. As a result, the XRF spectral dataset **152** includes characteristic peaks **166** of elements that uniquely identify the elemental composition of the region of interest **122** of the sample **104**.

FIG. **6A-6D** shows a workflow that illustrates the correlative aspects of the CT/XRF system **10**, for a feature of interest **120** selected by an operator within a tailings sample **104**. As in FIG. **4**, an operator uses the interactive graphic in

## 16

FIG. **6A** to select a feature of interest **120** within a slice **142**. The controller **128** calculates a region of interest **122** in response to the selection. The region of interest **122** includes the feature of interest **120**.

FIG. **6B** shows the XRF spectral data **152** obtained by the CXRF subsystem **102** for the region of interest **122** of FIG. **6A**. The controller **128** generates the XRF spectral data **152** as outlined in the description for FIG. **2** and FIG. **5**.

The controller **128** then correlates the volume information **150** with the elemental composition information **152** for the region of interest **122** to create and display elemental composition maps, such as the maps of FIGS. **6C** and **6D**. FIG. **6C** shows a map of the elemental distribution for the region of interest **122** as a function of depth, and FIG. **6D** shows a contour map of elemental iron (Fe) for the selected feature of interest **120**.

FIG. **7** displays the XRF spectral data **152** for a tailings sample **104** that includes Platinum (Pt) to show the sensitivity of the x-ray CT/XRF system **10**. The XRF spectral data **152** includes characteristic peaks **166** of different elements, such as metallic elements Iron (Fe), Chromium (Cr), Nickel (Ni), and Copper (Cu). Specifically, the XRF spectral data **152** includes characteristic peaks **166** of the Pt  $L\alpha$  line **162** and the Pt  $L\beta$  line **164**, the display of which is not possible using currently available XRF-only systems.

FIG. **8** shows more detail for the controller **128**. In examples, the controller **128** is a separate card of a computer system, or a stand-alone device. The controller **128**, in addition to other functions, manages the acquisition of volume information **150** on the x-ray CT subsystem **100**, and the acquisition of elemental composition information on the confocal XRF subsystem.

The controller **128** accepts the projection images **156** and calculates the volume information **150** from the x-ray CT subsystem **100**, and includes the interactive graphic **170** that enables operator selection of a synthetic slice **142** and feature of interest **120**. The controller **128** creates a region of interest **122** that includes the feature of interest **120**. The creation of the region of interest **122** depends on whether the x-ray CT subsystem **100** and CXRF subsystem **102** are part of an integrated system, or exist as separate, non-integrated systems.

In general, the resolution of the volume information/CT volume dataset **150** generated by the x-ray CT subsystem **100** is typically on the order of a few microns or less. In contrast, the resolution limit of current XRF systems is typically  $\sim(20\ \mu\text{m})^3$ . For the x-ray CT/XRF systems **10**, the controller **128** must account for the differences in resolution provided by the x-ray CT subsystem **100** and the CXRF subsystem **102**. As a result, the controller **128** creates a region of interest **122** of the volume information **150** that includes the selected feature of interest **120**, and additional voxels of the volume information surrounding the selected feature of interest **120**.

The controller **128** generates a coordinate transfer function **158** to convert CT system coordinates **204** ( $x, y, z, \theta$ )<sub>CT</sub> from the x-ray CT subsystem **100** to XRF system coordinates **207** ( $x, y, z, \theta$ )<sub>XRF</sub>. This conversion creates the region of interest **122** for the confocal XRF subsystem **102**. This conversion is also referred to as spatial calibration of the confocal XRF subsystem **102** based on the results of CT mode.

Once the controller **128** determines the region of interest **122**, the controller **128** provides the positions of the region of interest **122** to the CXRF subsystem **102** for acquisition of the elemental composition information **151**. The control-

ler **128** generates the XRF spectral dataset **152** as previously outlined in the description for FIG. **2** and FIG. **5**.

In a preferred embodiment, the controller **128** includes applications **138** that perform "offline" correlations between the volume information **150** and the XRF spectral datasets **152**. This enables generation of such correlated information as the FIG. **6C** 3-D elemental compositional plot as a function of depth, and the FIG. **6D** 2-D contour plot of specific elements. The controller **128** displays the XRF spectral datasets **152** and the correlated information to the display device **136**.

FIG. **9** illustrates an example of the steps for a calibration process of a CT/XRF system according to an embodiment of the invention.

In step **400**, a series of projections are acquired covering the reference sample at different angles. In one example, the reference sample includes at least three fiducial markers, also known as fiducials, in three different planes. This is required for unambiguous coordinate transfer. Preferably, the fiducial markers have high contrast in CT mode and are identifiable in XRF mode. In one example, high density spheres, such as 1-10  $\mu\text{m}$  diameter copper or gold spheres, function as fiducials. These fiducials are embedded in an epoxy matrix plug that functions as the reference sample. In another example, a cross-shaped fiducial is deposited on a membrane, that functions as the reference sample or target.

Then, in step **402**, CT volume data of the reference sample is generated from the projections. Next, in step **404**, the one or more fiducials are found in the reference sample using the CT volume data.

Depending on the type of CT/XRF system, the reference sample may need to be moved to the XRF system in step **406**, using a common kinematic mounting system. In step **408**, the sample is scanned to generate XRF data. In step **410**, fiducials are found in the reference sample using the XRF spectral data. The reference sample fiducials from the CT are compared with the reference sample fiducials of the XRF in step **412**. In step **414**, based on the step **412** comparison, a coordinate transfer function **158** is determined between CT system coordinates  $(x, y, z, \theta)_{CT}$  and XRF system coordinates  $(x, y, z, \theta)_{XRF}$ .

Before a mineral sample **104** is placed into a sample tube **110** for analysis by the CT/XRF system **10**, a pack of mineral material needs to be acquired and prepared.

FIG. **10** illustrates an example of the steps involved in converting mineral material to a mineral sample for analysis.

In step **500**, mineral material is mined. Then, in step **502**, the mineral material is crushed and ground into a powder. This mineral powder is run through a flotation process in step **504**. Flotation includes mixing the powder with detergent in an aqueous solution in order to separate mineral particles from the powder into the concentrate and tailings. Next, in step **506**, the raw mineral material and/or concentrate and/or tailings are packed into a sample tube **110**.

In step **508**, x-ray CT and confocal XRF analysis are performed on this mineral sample/concentrate/tailing **104** in the sample tube **110**. Based on the results of the x-ray CT/confocal XRF analysis, the mining/flotation process is modified and/or optimized in step **510**.

The analysis of a sample using a CT/XRF system is a process that can be run through separate CT and XRF systems as described in the method of FIG. **11A**, or through an integrated CT/XRF system as illustrated in the method of FIG. **11B**.

This process starts with a step **600/620** of acquiring a series of projections covering the sample **104** within the sample tube **110** at different angles. In step **602/622**, CT

volume data  $(x, y, z, \theta)_{CT}$  of the sample (e.g. mineral sample) are generated from the projections. This is accomplished using tomographic reconstruction algorithms that are executed by the controller **128**, for example.

Next, in step **604/624**, a user or computer algorithm executing on the controller **128** selects features of interest  $(x, y, z, \theta)_{CT}$  in the CT volume data.

In steps **606/626**, regions or volumes of interest are defined from the selected features of interest based on the CT volume data of the sample. In general, the resolution of the CT volume data is a few microns, or less. In contrast, the resolution limit of the XRF system under current technologies is  $\sim(20 \mu\text{m})^3$ . Thus, for each feature of interest that is identified in the CT volume data, a region of interest surrounding that feature is defined for the analysis executed by the XRF system.

If the analysis is performed using separate CT and XRF systems, step **608** includes the transfer of a sample tube to the XRF system after the regions of interest are defined. In step **610/628**, the selected regions of interest are positioned at the confocal probing spot of the XRF system by reference to the coordinate transfer function **158**. In step **612/630**, XRF spectral data from the regions of interest are acquired. The XRF spectral data are corrected using absorption information from the CT volume data in step **614/632**. Then, in step **616/634**, the XRF spectral data are matched with reference elemental information that correlates with elemental composition. Based on this match, the controller is able to identify the elemental composition of the regions of interest.

A raster scan analysis of the sample with a CT/XRF system can also be performed using separate CT and XRF systems as illustrated in FIG. **12A**, or an integrated CT/XRF system as illustrated in FIG. **12B**.

This process starts with step **700/720** of acquiring a series of projections covering the sample **104** within the sample tube **110** at different angles.

In step **702/722**, CT volume data  $(x, y, z, \theta)_{CT}$  of the sample (e.g. mineral sample) is generated from the projections. The sample is segmented from the CT volume data  $S(x, y, z, \theta)$  in step **704/724**. If the analysis is using separate CT and XRF systems, in step **706** the sample tube **110** is transferred to the XRF system after the sample is segmented in step **704**. Next, in step **708/726** surface points are raster scanned using segmentation with optimized rotation  $\theta$ . The sub-surface of the sample is raster scanned using segmentation in step **710/728**. In step **712/730**, the raster scan sub-surface step **710/728** is repeated to penetration limit.

The CT volume data are used to correct the XRF spectral data at depth using the transfer function to correlate CT volume data with XRF spectral data in step **714/732**.

FIG. **13** illustrates the process of determining the composition of the sample using CT and XRF systems.

In step **800**, the process starts with acquiring a series of projections covering the sample **104** within the sample tube **110** at different angles. CT volume data  $(x, y, z, \theta)_{CT}$  of the sample (e.g. mineral sample) is generated from the projections in step **802**. Next, in step **804**, the CT volume data are segmented into classes based on gray level. In step **806**, regions within each segmentation class are selected. Selected regions are positioned at the confocal probing spot of the XRF system in step **808**. In step **810**, the composition of the selected regions is determined. Then, in step **812**, a phase map  $(x, y, z, \theta)_{CT}$  of the sample is generated and the composition of the sample is determined using the composition information that is generated for each gray level in the CT volume data.

19

While this invention has been particularly shown and described with references to preferred embodiments thereof, it will be understood by those skilled in the art that various changes in form and details may be made therein without departing from the scope of the invention encompassed by the appended claims.

What is claimed is:

1. An x-ray computed tomography (CT)/x-ray fluorescence (XRF) system comprising:

a source for generating x-rays;

an x-ray CT subsystem for acquisition of volume information of the sample;

a confocal XRF subsystem for acquisition of elemental composition information including a source optical element that directs the x-rays received over range of angles from the source to generate a focused beam onto a region of interest of a sample located at a confocal probing spot of the confocal XRF subsystem; and

a controller in communication with the x-ray CT subsystem and the confocal XRF subsystem, wherein the controller manages the acquisition by the x-ray CT subsystem and the confocal XRF subsystem by selecting a number of points or areas predetermined from the volume information for the acquisition of elemental composition information by the XRF subsystem and placing the selected points or area at the confocal probing spot.

2. The system of claim 1, wherein the controller provides spatial calibration of the confocal XRF subsystem based on the volume information received from the x-ray CT subsystem.

3. The system of claim 1, wherein the controller combines the volume information from the x-ray CT subsystem with the elemental composition information from the confocal XRF subsystem to verify a liberation state of elements within a sample.

4. The system of claim 1, wherein the controller selects a limited number of points or small areas predetermined from the volume information for the acquisition of the elemental composition information by the confocal XRF subsystem.

5. The system of claim 1, wherein the controller performs correlation between the volume information and the elemental composition information to provide elemental contrast of a sample as a function of depth.

6. The system of claim 5, wherein in response to the correlation, the controller generates elemental distribution maps as a function of position within the sample.

7. The system of claim 1, wherein the controller: generates an interactive graphic, which enables the identification and selection of a feature of interest within the volume information acquired by the x-ray CT subsystem;

20

creates a region of interest that includes the feature of interest, the region of interest created to translate the feature of interest from x-ray CT subsystem coordinates to confocal XRF subsystem coordinates; and accesses the region of interest with the confocal XRF subsystem for the acquisition of the elemental composition information.

8. The system of claim 1, wherein the controller generates a coordinate transfer function that translates between x-ray CT subsystem coordinates and confocal XRF subsystem coordinates that accounts for differences in resolution between the x-ray CT subsystem and the confocal XRF subsystem.

9. The system of claim 1, wherein the controller generates a coordinate transfer function for translating selected features of interest from the volume information of the x-ray CT subsystem into a region of interest for acquisition of the elemental composition information by the confocal XRF subsystem.

10. The system of claim 9, wherein the confocal XRF subsystem positions the region of interest at a confocal probing spot of the confocal XRF subsystem by referencing the coordinate transfer function.

11. The system of claim 1, wherein the controller corrects the elemental composition information acquired by the confocal XRF subsystem using absorption information of the volume information acquired by the x-ray CT subsystem.

12. The system of claim 11, wherein the absorption information is associated with voxel intensities of the volume information.

13. The system of claim 1, wherein the controller compares the elemental composition information acquired by the confocal XRF subsystem against reference elemental information to identify elements in a sample.

14. The system of claim 1, wherein the confocal XRF subsystem selectively probes a region of interest of the volume information at a sub-micrometer spatial resolution for the acquisition of the elemental composition information.

15. The system of claim 1, wherein the source optical element is an optical polycapillary element.

16. The system of claim 1, wherein the confocal XRF subsystem further comprises a collection optical element having a focus that intersects a focus of the source optical element.

17. The system of claim 16, wherein the collection optical element is an elliptical polycapillary optic.

18. The system of claim 1, wherein the source optical element is switchable to be moved out of a path of the x-rays when the system is in CT mode and acquiring the volume information of the sample.

\* \* \* \* \*